University of Reading

Analysis of Soil Samples from Polluted Mining Areas

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Yuanyuan Wang

Department of Chemistry

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Declaration

I confirm that this is my own work and the use of all material from other sources has been properly and fully acknowledged.

Yuanyuan Wang

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Abstract

Soil is vitally important for life on Earth. Contamination of soil occurs all over the world and in many places mining activity has led to soil pollution. In this research a range of soil samples have been analysed. These were collected from two polluted mining areas in Wales: Hook Village and Parys Mountain. The overall aim of this project is to investigate the composition of the soil samples and to look at the leaching of metals from these soils. A further principal aim is to relate these findings to underlying physical properties such as the solubility of salts and the effect of pH on equilibrium. This project will also try to solve the questions such as the suitable conditions for metals to be leached out, the relationship between the minerals and metals present in the soil and the leaching of these metals and the role of humic acid in leaching metals from soil samples.

To determine the composition of the soil samples, different analytical methods and techniques have been used. From thermal analysis it is seen that soils from Hook Village have a higher percentage of both organic content (9.07 %) and carbonate content (pure $CaCO_3$: 3.10 % or pure $MgCO_3$: 2.60 %) than do soils from Parys Mountain (organic content: 4.41 %, pure $CaCO_3$: 1.45 % or pure $MgCO_3$: 1.21 %). Infrared Spectroscopy (IR) has been used to identify some of the minerals present in the soil samples. Quartz and clay minerals are present in both samples while Parys Mountain soils may contain a sulphate-containing mineral. From the results of X-ray Fluorescence, copper, lead, zinc, iron and some metals exist in the samples in higher concentrations than others and these metals were selected for the leaching experiments. Leaching experiments play the main role in this research. Different acids and different concentrations of acids were used as matrices to extract heavy metals from the soil samples. Chelating agents such as EDTA were also selected to compare with the acidification process. In addition to this, it is confirmed that humic acid can play an important role in the leaching of metal ions from soil samples but it is important to consider other factors such as the pH of the sample.

Contents

Chapter 1 Introduction

1.1 Background to contaminated soil sites

Soil is vitally important for life on Earth including the life of humans. Soil contamination affects both the health of humans and agriculture as a result of the entrance of heavy metals into the food chain and groundwater. Soil contamination can also affect the fertility of plants which in turn affects food production [1, 2, 3].

In many places, mining activity has led to soil pollution especially where heavy metals have contaminated the soil [4, 5]. In this research, soil samples collected from two polluted mining areas in Wales (Hook Village and Parys Mountain) have been fully characterised and analysed.

1.1.1 Soil samples from Hook Village

Hook village is a small village near Haverfordwest, which is located in Pembrokeshire, South Wales. This region of Pembrokeshire produced anthracite coal from mines ranging from Saundersfoot in the east to St Brides Bay in the west [6] and it had more than 200 coal mining sites at its peak activity in the 19th Century [7].

Figure 1.1.1.1 A satellite image of the area around Hook village, from google map

From the late 18th Century and early 19th Centuries there was coal mining near the village of Hook [8]. An anthracite colliery located around the western bank of the Cleddau estuary, opposite to Landshipping, was opened by Thomas Harcourt Powell around 1850. In 1880 the company was called the Hook Colliery Company. In 1896 there were 128 men employed at this site according to the list of Inspector of Mines. Coal was extracted at this site both by drift and shaft mining, reflected in its name of "Hook west, part pit". In 1918 a new drift was opened employing a further 69 men at the Hook new drift [9]. The Hook Colliery changed its name to Hook Anthracite Colliery Company in 1920. Three years later, there were 130 people employed at Hook pit. The colliery closed on 23rd of April 1948 on the nationalization of the UK coal industry [8, 10, 11]. In the late 20th century, the mining area became a residential area [8].

The coal mining activity has had some effects on the environment, agriculture, land use and waste management of the area. It may also have affected the health of local residents as it is likely to have caused water and air contamination. One aspect of this pollution may be acid mine drainage [12]. Coal mines and metal mines are often rich in sulphide minerals

such as pyrite (FeS_2) [13]. During or after the mining activity, sulphides are oxidized by water and air and then generate acidic water with high concentrations of suphate [14]. The chemical reactions are as follows:

$2FeS_2\,(s) + 7O_2\,(g) + 2H_2O\,(l) = 2Fe^{2+}\,(aq) + 4SO_4^{2-}\,(aq) + 4H^+\,(aq)$

The ferrous iron (Fe^{2+}) can be oxidized to ferric iron (Fe^{3+}) as follows:

$4Fe^{2+}\,(aq) + O_2\,(g) + 4H^+\,(aq) = 4Fe^{3+}\,(aq) + 2H_2O\,(l)$

The Fe^{3+} can react as an oxidant with water and pyrite to produce more Fe^{2+} and SO_4^{2-}:

$FeS_2\,(s) + 14Fe^{3+}\,(aq) + 8H_2O\,(l) = 15Fe^{2+}\,(aq) + 2SO_4^{2-}\,(aq) + 16H^+\,(aq)$

For this reason it is interesting to analyse the soil samples from the Hook Village coal mining area and to study the leaching of metals from these soils.

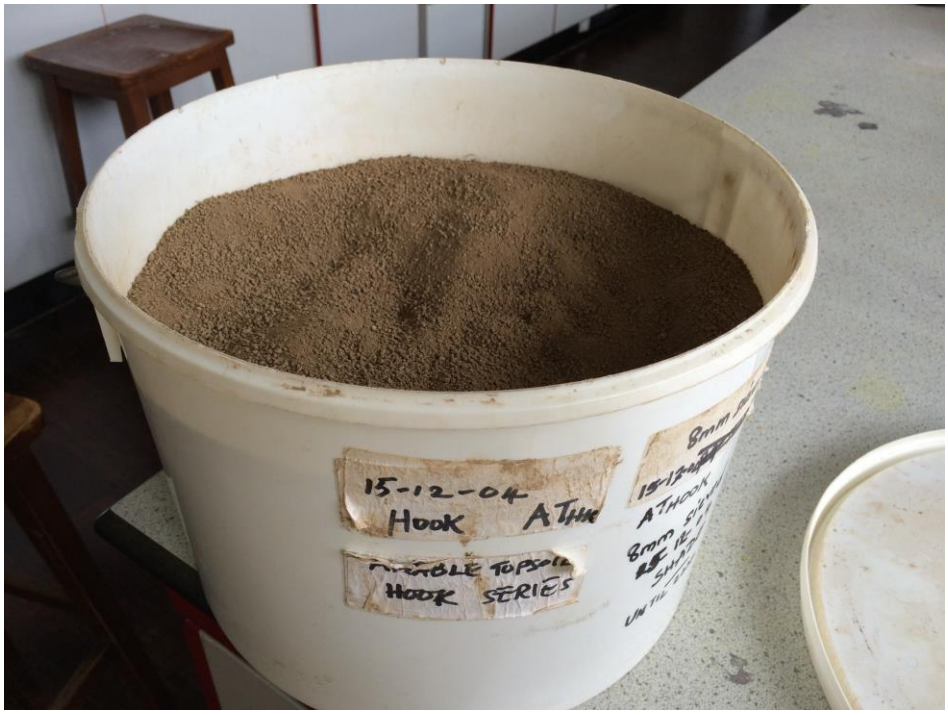

Figure 1.1.1.2 An image of the sample of soil from Hook village which was used in this research

1.1.2 Soil samples from Parys Mountain

Parys Mountain is situated south of the town of Amlwch in north east Anglesey, Wales.

Figure 1.1.2.1 A satellite image of the area around Parys Mountain, from google maps

Copper mining in parts of Parys Mountain has been carried out for thousands of years. There is evidence of Bronze Age activity and The Romans mined areas here for Pb and Cu. The first recorded work here was, however, in Elizabethan times (16th Century) [15]. It is therefore a site with very different mining activity and history from the site at Hook Village.

Parys Mountain is a site with a large copper mine which reached its peak activity in the late 18th century [16]. In 1761, the main phase of working began and Parys Mountain became Europe's premier copper mine. Since 1770 the mined veins have been extended into Parys

farm and the site supported two mines, Parys Mine in the west and Mona Mine in the east. In 1780, it was the largest copper mine in the world. Nearly 1200 people were employed and the output was more than 3000 tons of metallic ore a year [16, 17, 18]. But around 1830 most mining had ceased and many of the Mona mine's precipitation pits were abandoned [15]. This was largely a result of cheaper imported copper. In all nearly 3.5 million tons of ore have been extracted from this site producing 130000 tons of copper and there are still some parts of unextracted ore remaining on the hill.

Modern exploration of the site began in 1955. In 1973, 4.8 million tons of ore containing 1.5% copper, 3% lead, 6% zinc, and small amounts of gold and silver were still estimated to be present in this area [15]. In 2008, to develop the mining further, the Anglesey Mining Company negotiated with Western Metals of Australia but the venture failed because of the world metal prices at that time. There may well be future mining at this site given the recent worldwide rise in the price of copper [19]. In fact, the place currently still has resources of 2.11 million tons of ore containing Cu 0.58 %, Pb 2.18 % and Zn 4.11 % [19] in the indicated category and 4.11 million tons of ore containing Cu 1.46 %, Pb 1.2 %, Zn 2.4 % in the inferred category [20, 21]. The term "indicated" here means that an estimate has been made to a sample point and it has a reasonable level of confidence. And the term "inferred" here means the estimation has a low level of confidence.

There is therefore still a considerable amount of metal ore remaining at Parys Mountain and this project was designed to investigate whether this metal ore has some effects on the concentrations of heavy metals contained in the soil samples and how easily these metals can be leached from the soils. An overall aim of the project was to compare the two very different mining areas of Hook Village and Parys Mountain.

Figure 1.2.2.2 An image of the sample of soil from Parys Mountain which was used in this research

1.2 Introduction and Discussion of Previous Research in this Area

It is interesting to compare the soil samples from different kinds of mining areas. Hook Village has had coal-mining activity but is now disused while Parys Mountain has metal-ore mining activity and while disused still contains a significant amount of ore. In the following chapters, a wide range of analytical methods have been used to analyse the composition of the soil samples, especially the heavy metal content in the soil samples and to study the leaching of these heavy metals from the soil under a range of conditions. A more detailed discussion of the background to each chapter is given at the beginning of each chapter. However, a short, general overview is given here in order to explain the background to the various analytical techniques used in this research and to give some examples of the applications of these techniques. This introduction also places the work in

a wider context and indicates the impact of this research. Soil pollution, as mentioned previously, has potentially a very large influence on agricultural yields and on human health. Many of these problems arise from leaching of pollutants out of soils and, as such, an understanding of these leaching processes under a wide variety of conditions is of paramount importance. In order to understand these processes properly it is necessary to relate the leaching of metals to underlying physical principles such as solubility of salts, pH equilibria and redox equilibria. It is this specific point that is addressed in this research.

In the following sections a brief overview of the analytical techniques employed is given.

Thermal gravimetric analysis (TGA) is a simple and useful method to check the variation of several components within the soil samples by measuring the magnitudes of weight losses at different temperatures. In this research it was used to estimate the organic content of the soil samples and there are many examples where this method has been used to characterize soils with labile organic matter and to study organic matter evolution [22, 23] without any extraction step. In 2012, Gasco *et al.* confirmed that thermal analysis is a useful tool to evaluate the organic matter evolution of soils amended with sewage sludge [24]. Another example of the use of this technique is provided by Lau *et al.* who, in 2013, carried out an experiment to study bovine cortical bone by thermal gravimetric analysis [25]. They heated their samples at different temperatures and found that heat-treated bones had three stages of weight loss. When the temperature changed from room temperature to 160 °C, the weight loss was the water component. When the temperature changed from 200 °C to 600 °C, the weight loss is mainly due to the organic constituents. When the samples were heated at more than 600 °C, the organic constituents were decomposed and mineral phase loss started taking place until 850 °C. These findings are relevant to the research described in this thesis in that TGA has similarly been used in this work to estimate the water content, the organic content and the carbonate mineral content of soils samples by heating the samples to three different temperatures: water content (105 °C), organic content (450 °C) and carbonate content (950 °C). The details of this work can be seen in chapter 3.

Another very important parameter of soil samples which must be measured in research such as this is the pH value. It is known that when the pH value of the soil is too high or too low, it will affect food production. An example is provided by the work of Mulder *et al.* who in 1997 carried out experiments to show the negative effect of increasing soil pH on potato tuber yield [26]. Also, the pH value of the soil affects the metal solubility. Lower pH values of soils can enhance the solubility of heavy metals and this may have further effects upon agricultural yields as many of these heavy metals are toxic to plants [27]. Of course they are also toxic to animals (including humans) and so their presence in the food chain has the potential to cause problems for human health. In this research, in order to compare the effect of soil samples' acidity from Hook Village and Parys Mountain on the leaching of metals, pH measurements were made on the soil samples as a routine piece of analysis.

Infrared Spectroscopy (IR) can be used to identify molecules or ions or functional groups within a molecule. It may therefore provide information on the organic matter and minerals present in the soils samples [28]. As such it complements techniques which determine elemental content of soil samples which will be discussed later in this section.

In 1999, Ellerbrock *et al.* conducted research to characterize soil organic matter from a sandy soil [29]. These experiments were designed to determine whether or not the management practice of the soils affects the nature of the organic content. They used four different fertilizer treatments with the samples and they used Fourier Transform Infrared Spectroscopy (FT-IR) spectroscopy to obtain their results. They extracted the soil organic matter using two different methods: sodium pyrophosphate ($Na_4P_2O_7$) extraction with separation by centrifugation and precipitation with HCl and hot water extraction (heating under reflux for one hour) and separation. After extracting the soil organic matter, they studied the samples by FT-IR spectroscopy and the FT-IR spectra allowed the kind of functional groups to be determined. Their results by FT-IR confirmed that the composition of soil organic matter from samples was affected by the type of fertilization.

Another example to show the use of FT-IR to analyse soil organic matter is as follows. In 2015, Olsen *et al.* carried out research on compost carryover and the influence of this on

soil organic matter [30]. They also used FT-IR to investigate the soil organic matter and functional groups of compost. They found the soil organic matter showed enrichment which matched the composition of the added compost. IR spectroscopy was shown to be a very useful technique to monitor the enrichment and amendment of soil organic matter.

FT-IR can also used to study the mineral content of soils. In 2007, Tatzber *et al.* carried out an experiment designed to measure carbonate in soil and compared the FT-IR method with the standard, so called, Scheibler method [31]. The Scheibler method is to treat soil samples with HCl and connect them to gas tight Scheibler apparatus (this is an apparatus designed to measure the volume of gas evolved). Hence they measured the volume of the released CO_2 and used this to determine the calcium carbonate content. For their FT-IR studies they used KBr pellets. They confirmed the possibility of using the FT-IR method to measure the concentration of carbonates in soil samples. However they found a comparatively high error for both methods, possibly as a result of the inherent inhomogeneity of soil samples.

Another example of the use of IR spectroscopy is provided by the experiment carried out by Nayak *et al.* in 2007 [32]. They characterized the clays within a soil using a combination of X-ray fluorescence (XRF), X-ray diffraction (XRD) and FT-IR and they found that the clay contained alumina, silica, iron, calcium, magnesium oxide and other elements. FT-IR showed the presence of different minerals within the clays and XRD confirmed the presence of these minerals. XRF showed the chemical compositions such as Al_2O_3 and SiO_2 of the clay. The combination of XRD and FT-IR was shown to be very powerful in identifying the minerals present within the clays.

In the following research described in this thesis, IR was used to analyze the minerals present in the soil samples by observing the so-called “fingerprint” region (between 1350-400 cm^{-1}) where most of the characteristic absorbances of minerals such as carbonates, sulphates and silicates occur.

This research, however, has centred on the determination of metal concentrations both within the soils samples and when leached from the samples under a variety of conditions.

To determine the concentrations of metals, three different methods have been used: X-ray fluorescence (XRF), Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). XRF can provide qualitative and quantitative information on the elemental composition of the soil samples themselves [33]. It can determine different elemental concentrations from soil samples directly. AAS and ICP-MS can also be used to determine metals from soil samples. However, these two methods were used to study extractable elemental concentrations from leachates [33, 34]. AAS can usually only work with one selected metal at once as the light source has to be specific for each element, while the ICP-MS can determine multiple metals at the same time. A comparison was made of the results obtained by AAS and ICP-MS. In principle by comparing the results obtained for metal concentrations of the soils themselves (by XRF) and of the leachates (by AAS or ICP-MS) it is possible to determine the percentage of a particular metal that has been extracted under specific conditions. There are many examples in the literature of the use of these techniques to determine metal concentrations in soils and in leachates and a few of these experiments are discussed below.

In 2000, Boyle carried out experiments to study the precision, accuracy and detection limits of XRF to carry out rapid elemental analysis [35]. He used environmental materials such as soils and different sediments of known elemental composition to test the precision and accuracy of XRF. He found that the number of samples measured have more effects to the reliable characterization than the measurement precision or accuracy. Also, he found that major elements (Si, Fe, Ti, Ca, K and S) are determined with great precision. He reached the conclusion that XRF can provide rapid screening and accurate total elemental analysis with a large number of soil or sediment samples and it is useful in environmental research.

In 2008, Carr *et al.* evaluated the heavy metal pollution in soil of a sports ground in Galway City, Ireland where was formerly a rubbish dumping site with a portable XRF analyzer [36]. They found that the soil pollution with Pb, Cu, Zn and As was serious as the concentrations of the four metals were extremely high. Their study also demonstrates the

effectiveness of using a portable XRF metal analyser for contaminated soils as they completed a study of 200 grid locations within 5 days of field work.

In the past, many studies have been performed to compare the results when using different analytical methods to analyse the samples. An example is provided by the work of Djingova *et al.* who in 1998 carried out the experiments to compare the results collected by XRF and AAS in the analysis of plants [37]. They found that XRF analysis cannot be used very successfully for all the elements from the plants and only limited number of elements such as Fe, Zn, Pb, Br and Cu gave good results. They also reached the conclusion that AAS is suitable to determine particular heavy metals such as Pb, Cd and Cu.

Another comparison example of XRF and AAS has been made by Ernst *et al.* in 2003. They used AAS and XRF to analyse the metals in printed wiring boards [38]. They extracted the samples using aqua regia and measured the concentrations of the extracted elements by AAS then compared the results with those from XRF. They found that although there were some limits, such as the small sample volumes, which restricted the precision, XRF is a convenient and quick measurement while AAS was very suitable for the quantification of single elements in the extract.

In 1997, Chung *et al.* conducted research to determine trace levels of toxic elements in Korean rice by ICP and AAS and they compared these results with results that they obtained using instrumental neutron activation analysis [39]. They found that the data from AAS and ICP-MS are very similar but that some values from neutron activation analysis were rather lower than those obtained by AAS or ICP-MS. This means that there is good correlation between the detection methods of AAS and ICP-MS for these samples of Korean rice.

In 2002, Vazquez *et al.* determined the concentrations of 28 elements in samples from various sites on the upper reaches of River Nysa (in Eastern Europe) and compared the results obtained by ICP-MS and AAS [40]. The results showed that the concentrations of elements in samples showed no significant differences when determined by the two

techniques, but that there were small specific differences in some measurements dependent on the specific element being measured.

However, the results obtained by the two different methods of ICP-MS and AAS are not always the same. In 2011, Frankowski *et al.* carried out an experiment to determine the aluminium in ground water samples by AAS, ICP-AES (Inductively Coupled Plasma atomic emission spectrometer) and ICP-MS [41]. The results collected from the different analytical techniques were compared. They found the results obtained using AAS were statistically different from the results obtained from the ICP-MS. They suggested a hypothesis that the differences may have been caused by the different injection systems for the ICP and AAS techniques. As part of the current research described in this thesis a comparison is made between AAS and ICP-MS for leachates obtained from soil samples.

The principal part of the research in this thesis is leaching experiments in which selected heavy metals from the soil samples were analysed. Leaching was studied under a wide variety of conditions. Different concentrations of inorganic acids and different chelating agents were used to obtain the leachates. All of the leachates were measured by AAS to get a comparison; some leachates were also measured by ICP-MS.

1.3 Aims and objectives of the research

The overall aim of this project is to investigate the composition of the soil samples from different mining areas and to look at the leaching of metals from these soils. A further principal aim is to relate these findings to underlying physical properties such as the solubility of salts and the effect of pH on equilibrium.

This project will also try to answer the following specific research questions:

1. How does the soil composition vary from site to site?

2. What specific metals contaminate the soils and what are the concentrations of these metals?

3. What is the relationship between the minerals and metals present in the soils?

4. What are the suitable conditions for metals to be leached, and what proportion of different metals is leached under different conditions?

5. Does the amount of metal leached from an individual soil sample increase as the acidity increases?

6. If acids with different anions but with the same acidity are used, do they have the same efficacy of soil leaching?

7. How do chelating agents work in the leaching process and how efficient are they at leaching different metal ions?

8. What role does humic acid play in leaching metals from soil samples?

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Chapter 2 Experimental

2.1 Introduction

In this research, a wide range of analytical techniques have been used to analyse the soil samples from two environmentally-important sites, Hook Village and Parys Mountain, which in the past were mining areas. This chapter outlines the analytical methods and techniques that have been used. They include thermal analysis, pH measurement, infrared spectroscopy, X-ray fluorescence spectroscopy, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry and particle size analysis.

Table 2.1 Multiple methods to analyse the soil samples

Methods	Purpose
1. Thermal analysis	To determine water content, organic content and calcium carbonate content from soil samples.
2. pH measurement	To determine the pH value of the soil samples.
3. Infrared Spectroscopy	To analyze the minerals present in the soils samples.
4. X-ray Fluorescence Spectroscopy	To determine the concentrations of different elements from soil samples.
5. Atomic Absorption	To analyze the concentrations of selected metals (Cu,

Spectroscopy	Zn, Pb and Fe) from soil sample leachates.
6. Inductively coupled plasma mass spectrometry	To analyze the concentrations of multiple trace metals from soil sample leachates.
7. Particle size analysis	To determine the particle size distribution of soil samples.

2.2 Thermal gravimetric analysis

2.2.1 Background

Thermal gravimetric analysis (TGA) is a useful method to investigate soil samples [1]. When samples are heated, chemical and physical changes will occur. The magnitudes of weight losses at different temperatures allow the content of various components to be determined. In this research, TGA has been used to determine the water content, organic content and calcium carbonate content in soil samples.

2.2.2 Method

The soil samples contained in weighing bottles were weighed using a four-figure balance (GEC AVERY, Model: YA124-1AAZM13AAA-120 g*0.0001 g).

To determine the water content of the soil samples, the samples were put into the vials and placed in an oven at 105 °C. After heating for 24 hours, they were removed from the oven and weighed again. The samples were placed back into the oven and heated at the same temperature until the weight remained constant (typically 72 hours).

To determine the organic content of soil samples, the samples were contained in crucibles and placed in a muffle oven at 450 °C [2]. As the space inside the oven is limited, the soil samples from different sites were put into different ovens. But all the samples were heated at the same temperature, for the same time period, and on the same dates. For the soil samples from Hook Village, a muffle oven of Lenton Thermal Designs Ltd. CAL90 was used and for the soil samples from Parys Mountain, a muffle oven of Lenton Thermal Designs Ltd. Eurotherm 91e was used. The samples had already been heated at 105 °C to remove water. The crucibles had already been heated at 105 °C to remove water to get a dry weight. The samples were cooled in a desiccator before weighing. The organic matter is oxidized according to the equation:

$$CxHy\,(s) + (x + y/4)\,O_2\,(g) \rightarrow x\,CO_2\,(g) + y/2\,H_2O\,(g).$$

To determine the carbonate content of soil samples, the samples were contained in crucibles and heated at 950 °C [3](muffle oven Lenton Thermal Designs Ltd. CAL 9500). The samples had already been heated to 450 °C to remove water and organic matter. The samples were cooled in a desiccator before weighing. The relevant equation is:

$$MCO_3\,(s) \rightarrow MO\,(s) + CO_2\,(g).$$

Thus for every mole of MCO_3, one mole of CO_2 (ca. 44 g) is lost.

2.3 pH measurement

The results of thermal analysis (details can be seen in chapter 3.2.1), after heating for 72 hours give a reliable estimate of water content from soil samples. However, the water content of soil samples is variable and so in this research all soil samples were dried in oven at 105 °C for 72 hours before further analysis was carried out.

The pH measurements were made using a Jenway 3020 pH meter. In order to compare the effect of soil samples' acidity for leaching experiments, the pH measurements were made on the soil samples under two different conditions and the findings were compared. For the first determination, about 0.5 g of soil from each site was stirred with 20 ml of deionised water for half an hour. The pH of the solution was measured using the pH probe mentioned above. For the second determination, about 2 g of soil from each site was stirred with 20 ml of deionised water for half an hour and the pH of solution was measured.

2.4 Infrared Spectroscopy

2.4.1 Background

Infrared Spectroscopy (IR) absorption can be used to identify molecules or ions or functional groups within a molecule. It is also used to provide identification and quantitative measurements of compounds [4]. Analytical infrared studies are based on the absorption of electromagnetic radiation in the infrared region [5, 6]. The absorption is quantized and certain frequencies of IR radiation are absorbed corresponding to molecular

vibrations of the molecule or ion under investigation. The region between 1350- 400 cm^{-1} is known as the "fingerprint" region. For instance, the IR absorption spectrum provides a fingerprint for molecules with covalent bonds which may be compared with the spectrum of an authentic sample. A typical example is the (Si-O-Si) group of silicates and clays which in compounds gives an absorption band close to 1015 cm^{-1} from the υ(Si-O-Si) stretching vibration and a band close to 540 cm^{-1} from bending modes. Quartz is a crystalline form of silica (SiO_2) and this shows an absorption band at 778 cm^{-1} arising from a bending mode. By contrast a peak at 797 cm^{-1} indicates that amorphous silica is present [7]. Another example is a peak at 428 cm^{-1}. It is the absorption peak of iron ore (Fe_2O_3) arising from a υ(Fe-O) mode [8]. The IR spectrum also can show the presence of a given functional group in organic compounds, such as carbonyl group (C=O, *ca.* 1700 cm^{-1}) and comparison of spectra in the fingerprint region is often used to identify an organic compound.

In this research, IR was used to analyze the composition of the soil, especially the minerals present in the soil.

2.4.2 Method

Each soil sample was thoroughly dried. A small amount of soil was taken by a spatula and ground with a pestle and mortar. A background scan was taken so that the background could be subtracted. Then the sample powder was placed onto the ATR (Attenuated Total Reflectance) attachment of an infrared spectrometer (model: PerkinElmer Spectrum 100 FT-IR spectrometer, working at room temperature) and the spectrum was recorded using 32 scans.

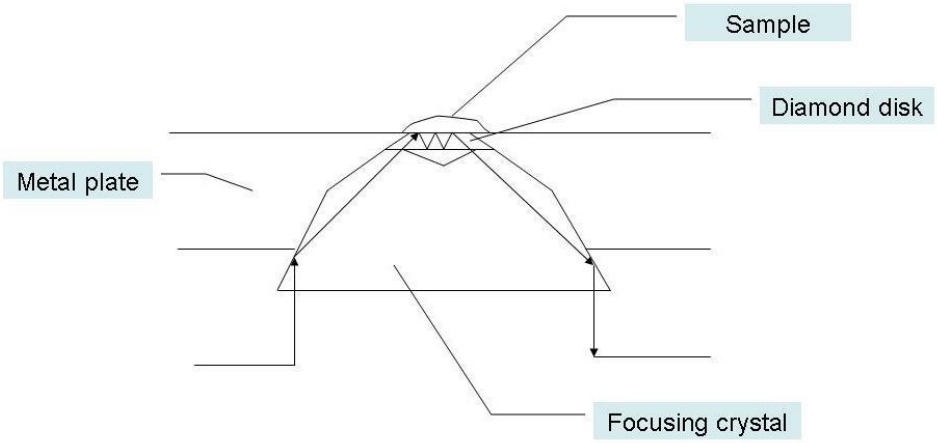

Figure 2.4 Diagram to show the path of the IR beam through the sample by PerkinElmer Spectrum 100 FT-IR spectrometer with ATR attachment

An IR beam was passed through a focusing crystal (eg. ZnSe) and reflected at the interface between sample and diamond disk [1, 9]. The instrument recorded spectra quickly as sample preparation was not necessary for most samples.

2.5 X-ray Fluorescence Spectroscopy

2.5.1 Background

X-ray fluorescence (XRF) can provide qualitative and quantitative information on the elemental composition of the samples [6]. Although XRF only looks at the surface of the samples, it can give precise concentrations of the different metals present on that surface simultaneously. For all elements, fluorescence appears in the broad energy range from

40eV to more than 100keV [5]. XRF works on the principle that when an atom of an element is bombarded with high energy X-rays core electrons are ejected from the atom. Electrons from higher energy levels fill the "holes" that are created in this way and X-rays are emitted. As the energy levels for each element are different the energy (and hence the wavelength) of the ejected X-rays will be characteristic of each individual element [10].

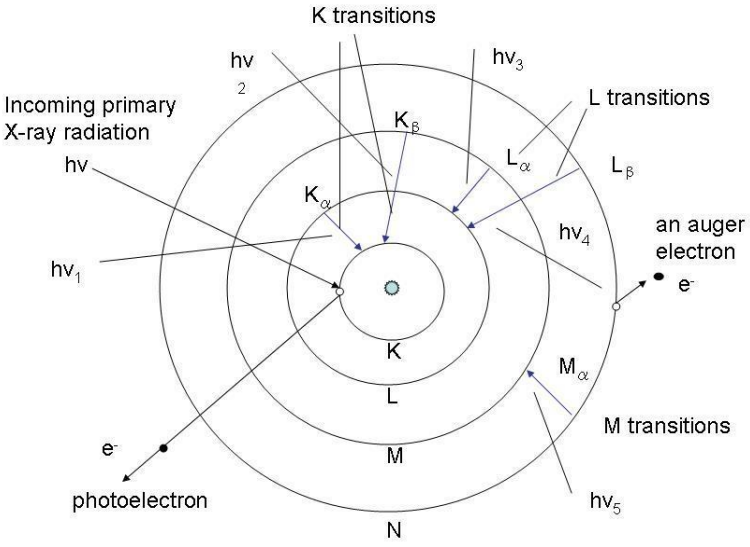

Figure 2.5.1 A Schematic Diagram of the X-ray fluorescence process redrawn from reference [5]

Moseley's Law [11] shows the relationship between wavelength for characteristic X-ray lines and atomic number. The wavelength is inversely proportional to the atomic number.

Moseley's Law: $\upsilon = c/\lambda = a(Z-\sigma)^2$

Where c = speed of light, λ = the wavelength of the X-ray, a = a constant for a particular series of lines (e.g. K_α), Z = the atomic number of the element, σ = a screening constant

that accounts for the repulsion of other electrons in the atom.

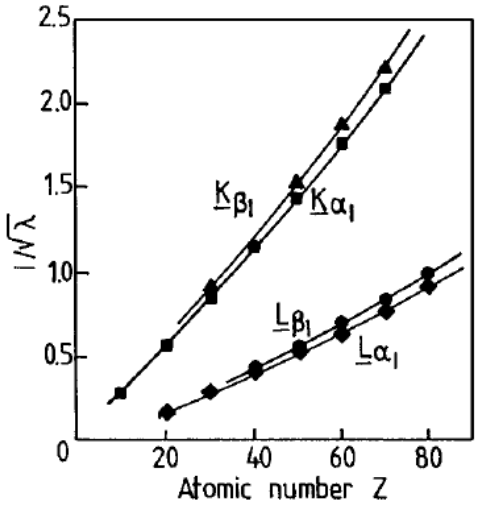

Figure 2.5.2 Partial Moseley's Law plots for selected K and L lines copied from reference [1]

2.5.2 Method

A small quantity of each sample was ground and shaken until homogeneous. Then the soil sample was put into a mould. Pressure was applied to make the surface smooth. Boric acid was added to the soil and the two parts were then pressed into a disc. The disc was used to measure the X-ray fluorescence spectrum by using a Philips PW 1480 X-ray Fluorescence Spectrometer.

2.6 Leaching

2.6.1 Background

Leaching experiments play a main role in this research. Leaching tests are fundamental tools for the assessment of contaminated soil. Generally, acidification is a useful process to promote leaching of heavy metals from contaminated soil [12]. Acidification can be carried out by mixing samples with acid. This process is called chemical leaching. After leaching, the concentrations of metals can be determined by different instruments such as atomic absorption spectroscopy or inductively coupled plasma mass spectroscopy [5, 13].

2.6.2 Method

When doing leaching experiments, the pH value and stirring time should be controlled as they are all very important parameters. In this project, the agitation time has been fixed as 24 hours and the pH value has been controlled by using certain concentrations of acid.

Dry soil samples (0.5 g) were weighed and put into conical flasks (50 mL). Four samples from each site have been taken as replicates to get an average of the results. Different solutions were selected as matrices. Each matrix solution (20 mL) was added to the flask with the weighed soil sample and was labeled with the name of the site and of the matrix. The solution was circulated through the soil for 24 hours before the sediments were filtered. A magnetic stir bar was added to each flask and the samples were left stirring (Fisher Scientific, Heating magnetic stirrer FB15001, room temperature). Each flask was covered by clear film to reduce evaporation. Leachates were first filtered through Buchner funnels with No.1001-055 filter paper (Whatman, 55 mm Φ). Then filtrates were sieved again

using a 0.45 μm membrane (Sartorius stedim minisart) with Plastipak 10 mL syringes (REF 302188) to remove fine particles which could interfere with the operation of the instrument (Atomic Absorption Spectroscopy) used for analysis of the solutions.

2.7 Atomic Absorption Spectroscopy

2.7.1 Background

An Atomic Absorption Spectrometer (AAS) contains four principal components:

1. A burner assembly to produce the flame

2. A system to aspirate the sample into the flame

3. A lamp to emit light at the appropriate wavelength for the element being analyzed

4. A detector [5].

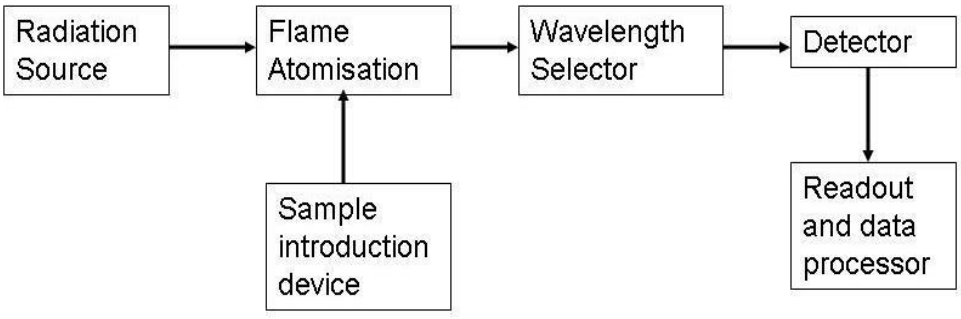

Figure 2.7.1 Block diagram of the components of an AAS

In AAS a light source is used to irradiate atoms of the elements under investigation in a flame. The wavelength of the light is such that absorption takes place by the atoms and some of the light is absorbed. The fraction of light absorbed depends on the concentration from the Beer-Lambert law: $A = \varepsilon lc$ [1]

Where A = absorbance, ε = molar extinction coefficient (or molar absorptivity), l = path length and c = concentration.

2.7.2 Method

In this research, a Nov AA 350 Analytik Jena instrument was used to analyse copper, iron, zinc and lead from the samples at room temperature. Standards for each element were prepared to calibrate the instrument. In some cases the samples required further dilution as the absorption readings were higher than the range of detection of the instrument. From the standard curve, from absorption reading the concentration of each leachate "x" can be found. As the leachates are from 0.5 g soil samples with 20 mL matrix, the concentration of metals can be calculated.

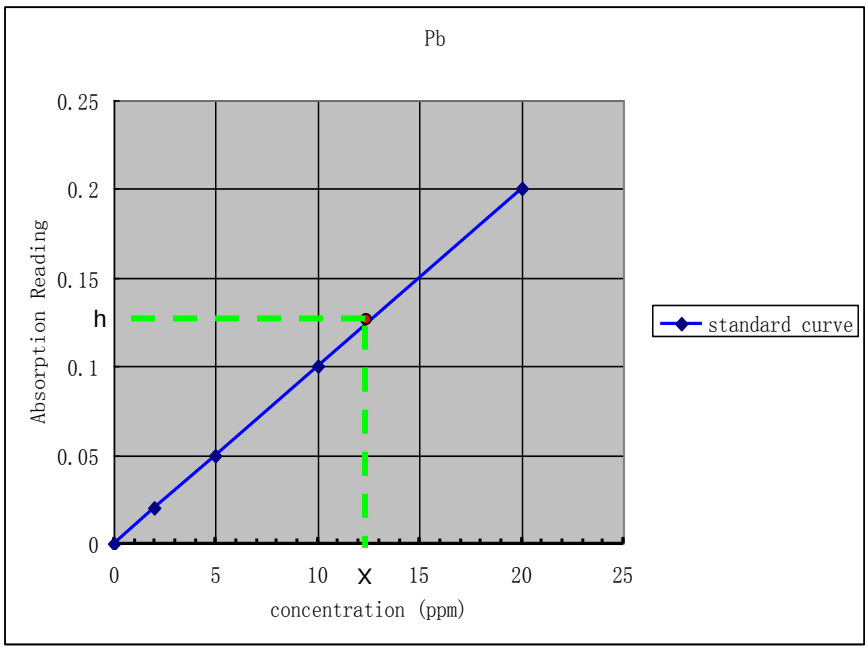

Figure 2.7.2 An example of the calculation of the concentration of a particular element (in this case Pb) from the absorption readings using a calibration curve.

2.8 Inductively coupled plasma mass spectrometry

2.8.1 Background

Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) can be used to determine extractable elemental concentrations from leachates [13, 14]. An ICP-MS combines a high temperature ICP source with a mass spectrometer. The ICP source atomizes and ionizes the elements in the sample. The ICP has high ionization efficiency and it produces singly-charged positive ions [5]. The elements can be identified from their masses and the isotope ratios can be measured by the mass spectra.

ICP can give quantitative information of the concentration of metals present in the samples. ICP is used routinely to determine ppb and ppm concentrations of most metal elements. An advantage of ICP-MS is that many elements can be determined at one time whereas in AAS a different light source is needed for each element which is determined as the light source has to be specific for each element.

2.8.2 Method

In this research, a Thermo Scientific^{TM} iCAP^{TM} Q ICP-MS instrument and ASX-520 autosampler instrument were used to analyse ten different heavy metals (V, Cr, Co, Ni, Cu, Zn, Sr, Zr, Pb and Fe) from the samples at room temperature at the same time.

Dry soil samples (0.5 g) were weighed and put into conical flasks (50 mL). Four samples from each site have been taken as replicates to get an average of the results. Four different solutions (0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, 0.1 M EDTA-2Na,) were selected as matrices. After the leaching process (the same step as in 2.6.2), all the leachates were diluted 100 times by 2 % HNO_3 solution with 5 ppb Rh added as an internal standard. A standard solution with a mixture of the metals analysed was also made up in 2 % HNO_3 with 5 ppb Rh added as a calibration. As the concentration of Fe was so high, all samples were diluted 5000 times to avoid overloading the detector. All the standards and samples were loaded directly into an autosampler to run.

Figure 2.8 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

2.9 Particle size analysis

2.9.1 Background

Particle size analysis plays an important role in the analysis of soil samples. Laser Granulometry can be used to determine the particle size distribution of sediments within the range of 0.04 μm to 2000 μm [15, 16, 17]. The principle of this method is that a lens is positioned in a laser beam path before the beam enters the sample cell containing the soil as a suspension. With no particles in the sample cell, light is refracted through the lens. When particles are present in the sample cell, light is diffracted by the individual particles at an angle that is dependent on the particle size [18, 19]. The larger is the particle the smaller the angle of diffraction [20, 21]. The angle of diffraction also depends on the wavelength of the incident light – hence the use of two light sources in this experiment to cover the whole range of particle sizes [22].

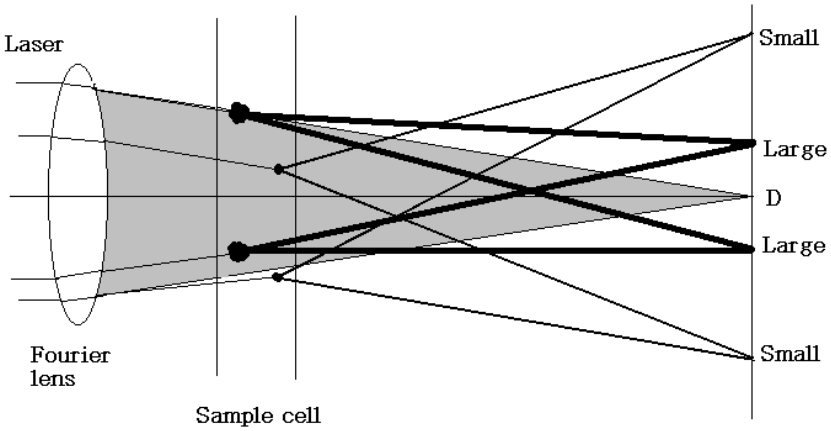

Figure 2.9.1 Diagram to show the different angles when the laser through the sample cell diffracted by the individual particles

2.9.2 Method

In this research, Malvern Mastersizer 3000 (Model: MA 23000, at room temperature) was used to study the particle size of the soil samples.

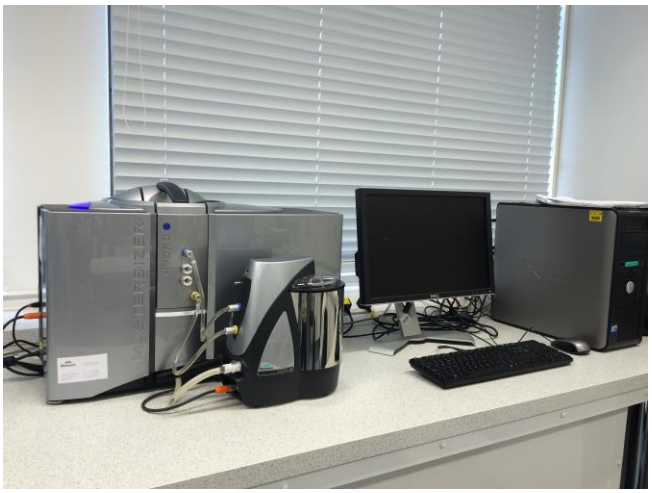

Figure 2.9.2 Malvern Mastersizer 3000

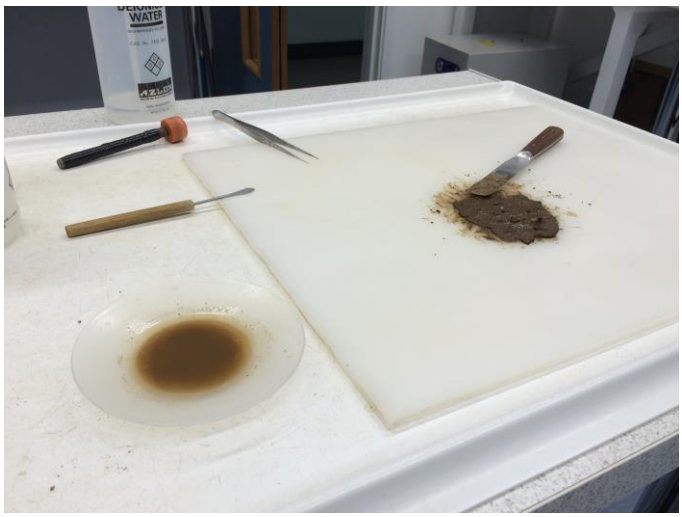

Figure 2.9.3 Picture showing the preparation of samples for particle size analysis

10 g of each soil sample was prepared on a Teflon sheet and mixed by spatula with a small amount of deionised water to form a homogenous sediment. A diamond shaped implement was used to collect small portions of the spread sample and to transfer the soil onto a plastic plate. A few drops of dispersant solution “calgon” (3.3 % sodium hexametaphosphate + 0.7 % sodium carbonate in deionised water) was added into the plate to disperse the particles [15, 23]. A rubber pestle was used to disaggregate the sample [14]. A few drops of deionised water were added to let the sample form into a fine-grained “muddy” sediment [15, 23]. Any particles observed to be greater than 2 mm were removed. The “muddy” sample was washed into the instrument Mastersizer 3000 by deionised water. The sample was suspended in the instrument and it was continuously pumped through the PIDS (Polarisation Intensity Differential Scattering) sample cells and the scattered light was detected.

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Chapter 3 General Analysis of Soil Samples

3.1 Introduction

Soil is vitally important for life on Earth including the life of humans. As mentioned previously soil contamination may affect the health of humans and agriculture [1, 2, 3]. In many places soil pollution has resulted from mining activity and the aim of this chapter was to investigate the pollutants present in a number of soil samples from Hook Village and Parys Mountain. In addressing this aim a number of specific objectives were to be considered. These are addressed via the following research questions:

1. How does the soil composition vary from different site?

2. What specific metals contaminate the soils and what are the concentrations of these metals?

3. What is the relationship between minerals and metals present in the soils?

In this chapter, a range of different methods have been used to determine the composition of soil samples. Firstly, soil samples were characterized by thermal gravimetric analysis to determine water content, organic content and calcium carbonate content [4]. The pH value was measured by pH meter. Infrared Spectroscopy has been used to analyze the minerals present in the soils [5, 6]. The composition of the soil samples was further analyzed using X-ray Fluorescence (XRF) to determine the elemental concentrations [7]. Leaching tests are fundamental tools for the assessment of contaminated soil. Leaching experiments were carried out under different conditions and inductively coupled plasma mass spectrometry (ICP-MS) and Atomic Absorption Spectroscopy (AAS) were used to analyze the leachates. The physical properties of soil samples such as particle size may affect retention of heavy

metals in the leaching process [8]. To investigate how physical conditions of a soil affect leaching, ground and unground soil samples have been selected for leaching with the same matrices. Particle size analysis has also been used to determine the particle size distribution of sediments.

For the reason that soil is a non-homogeneous substance, at least four replicates of analyses of soil samples from each site were performed and the results are expressed as an average. Extra repeat experiments also have been done to test the repeatability of the method.

3.2 General analysis

3.2.1 Thermal gravimetric analysis

3.2.1.1 Determination of water content by thermal analysis

The water content in the soil samples is always affected by the weather and air humidity. It can never show a stable value. So the following research was done on dry samples. First, determination of water content by thermal analysis has been done.

Although soil samples are always inhomogeneous, using more samples to determine water content can give an idea of the range of water content and may give a better average. From each site, ten samples have been chosen and heating was carried out for more than 96 hours to make sure all the water content has been measured.

The following two figures show the water content of soil samples from two selected sites after heating to 105 °C.

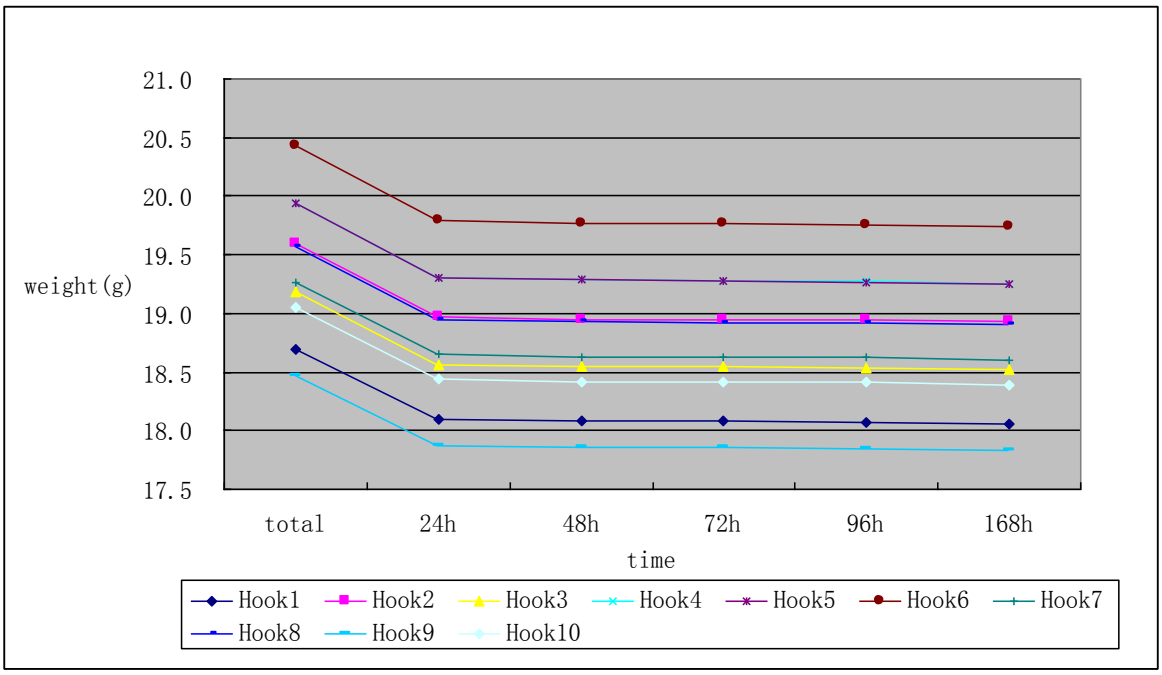


Figure 3.2.1.1.1 Determination of water content of soil-samples from Hook Village by measurement of weight loss from soil at 105 °C

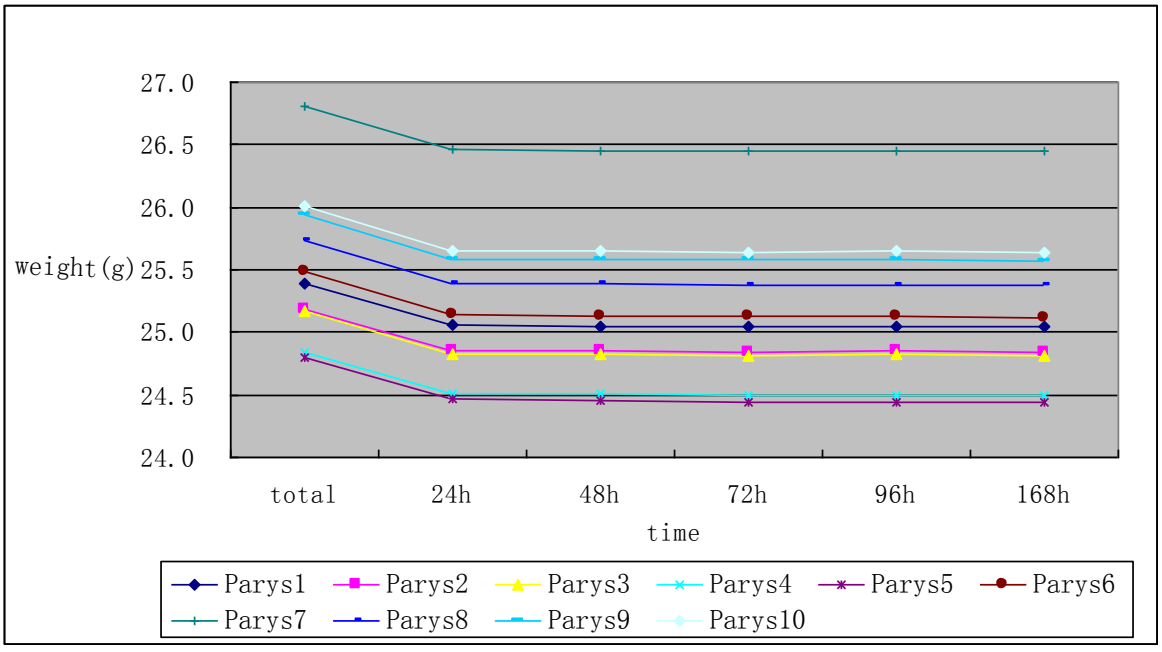


Figure 3.2.1.1.2 Determination of water content of soil-samples from Parys Mountain by measurement of weight loss from soil at 105 °C

Table 3.2.1.1 Water content of soil samples from Hook Village and Parys Mountain

Hook Village		Parys Mountain	
Sample name	mass loss after heating 168 hours (%)	Sample name	mass loss after heating 168 hours (%)
Hook 1	3.40 %	Parys 1	1.39 %
Hook 2	3.39 %	Parys 2	1.38 %
Hook 3	3.44 %	Parys 3	1.42 %
Hook 4	3.44 %	Parys 4	1.41 %
Hook 5	3.42 %	Parys 5	1.48 %
Hook 6	3.36 %	Parys 6	1.42 %
Hook 7	3.39 %	Parys 7	1.34 %
Hook 8	3.40 %	Parys 8	1.40 %
Hook 9	3.40 %	Parys 9	1.44 %
Hook 10	3.43 %	Parys 10	1.45 %
Average	**3.41 %**	**Average**	**1.41 %**

From the chart it is clear that after 24 hours heating, the weight of soil sample changes very little, and after 48 hours heating, the changes of weight are minimal as the graphs show

very nearly a straight horizontal line. (Full details can be seen in Appendix.)

Hook Village: this sample contains 3.41 % ± 0.025 % of water.

Parys Mountain: this sample contains 1.41 % ± 0.039 % of water.

3.2.1.2 Determination of organic content by thermal analysis

The organic content of soils is very variable. Some soil can contain 20% or 30% organic content such as peat soil or some soils from forests. Some soil can contain just 1% or 0.5% organic content such as desert soil or Aeolian sandy soil [9]. Organic content will affect the results of leaching experiments [10], so measuring the organic content of each sample is important in order to explore any relationship between the mobility of the metals and the composition of the soil.

In this step, all the samples have been heated initially for more than 72 hours to remove water (Table 3.2.1.1). Then the following organic content of each dry sample was determined.

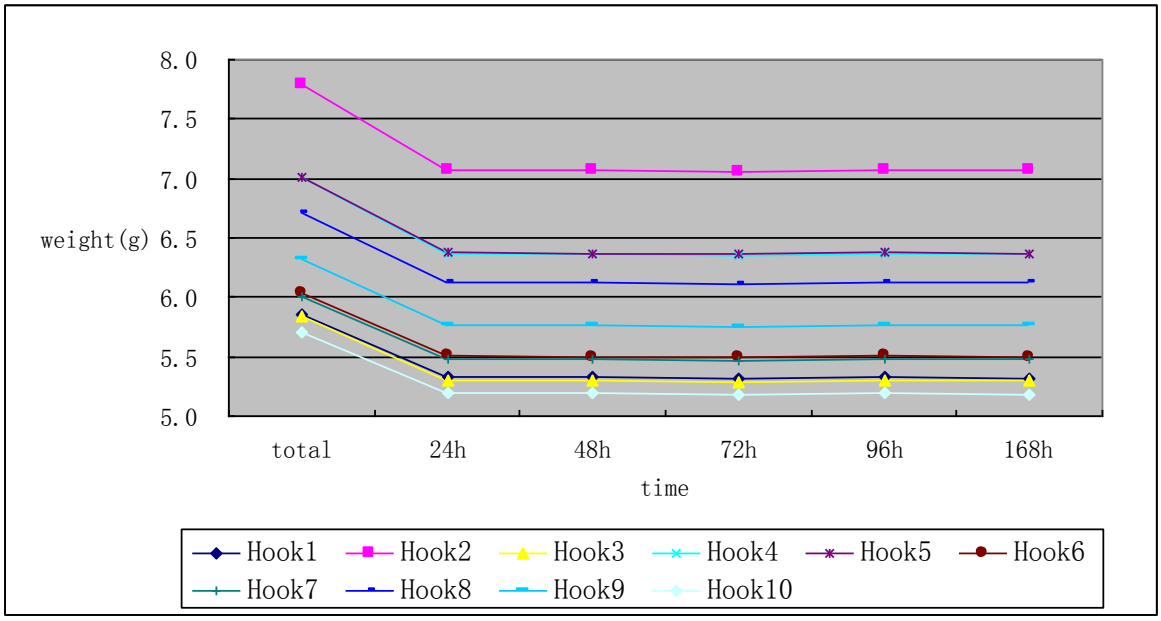


Figure 3.2.1.2.1 Determination of organic content of soil-samples from Hook Village by measurement of weight loss from soil at 450 °C

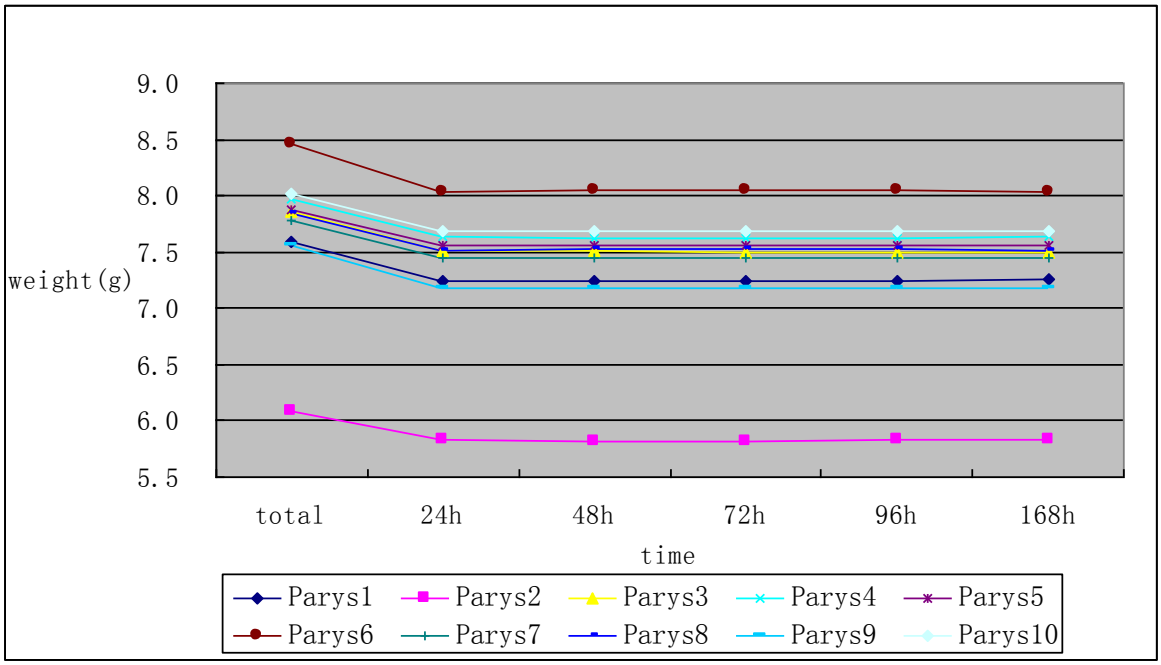


Figure 3.2.1.2.2 Determination of organic content of soil-samples from Parys Mountain by measurement of weight loss from soil at 450 °C

Table 3.2.1.2 Organic content of soil samples from Hook Village and Parys Mountain

Hook Village		Parys Mountain	
Sample name	mass loss after heating 168 hours (%)	Sample name	mass loss after heating 168 hours (%)
Hook 1	9.16 %	Parys 1	4.51 %
Hook 2	9.26 %	Parys 2	4.13 %
Hook 3	9.26 %	Parys 3	4.49 %
Hook 4	9.28 %	Parys 4	4.23 %
Hook 5	9.09 %	Parys 5	3.97 %
Hook 6	8.93 %	Parys 6	4.95 %
Hook 7	8.83 %	Parys 7	4.20 %
Hook 8	8.87 %	Parys 8	4.25 %
Hook 9	8.94 %	Parys 9	5.14 %
Hook 10	9.04 %	Parys 10	4.18 %
Average	**9.07 %**	**Average**	**4.41 %**

All the samples were cooled to room temperature in a desiccator before weighing. All the crucibles have been weighed after heating to the same temperature (450 °C).

From the chart it is clear that after 24 hours heating, the weight of soil sample changes very little. So the results of heating for 72 hours give a reliable estimate of organic content.

Hook Village: 9.07 % ± 0.17 % of the sample is organic matter.

Parys Mountain: 4.41 % ± 0.38 % of the sample is organic matter.

3.2.1.3 Determination of carbonate content by thermal analysis

The determination of carbonate content is an important part of soil analysis, as the concentration of carbonate is likely to affect the results of leaching experiments and will affect the pH of a soil sample. When acidification takes place [11], the solubility of carbonate will change as demonstrated by the following equilibria:

$MCO_3\,(s) \leftrightharpoons M^{2+}\,(aq) + CO_3^{2-}\,(aq)$,

$CO_3^{2-}\,(aq) + H^{+}\,(aq) \leftrightharpoons HCO_3^{-}\,(aq)$,

$HCO_3^{-}\,(aq) + H^{+}\,(aq) \leftrightharpoons H_2O\,(aq) + CO_2\,(g)$.

Thus acidification will tend to dissolve the carbonate and therefore make any metal ions combined as metal carbonates more mobile [12, 13]. The carbonate content of each sample was measured by thermal analysis and some “spike” experiments have been done such as add addition of calcium carbonate. In the “spike” experiments, different amounts of calcium carbonate were added to the original soil samples and leaching experiments were carried out with the spiked samples to check whether the additional calcium carbonate affects the leaching results (details can be seen in chapter 4 - 4.6 and chapter 5 - 5.4).

If it is assumed that all of the carbonate content is from calcium carbonate, to determine

the calcium carbonate content of soil samples by thermal analysis, the relevant equation is:

$CaCO_3$ (s) → CaO (s) + CO_2 (g).

Thus for every mole of $CaCO_3$ (ca. 100 g) one mole of CO_2 (ca. 44 g) is lost.

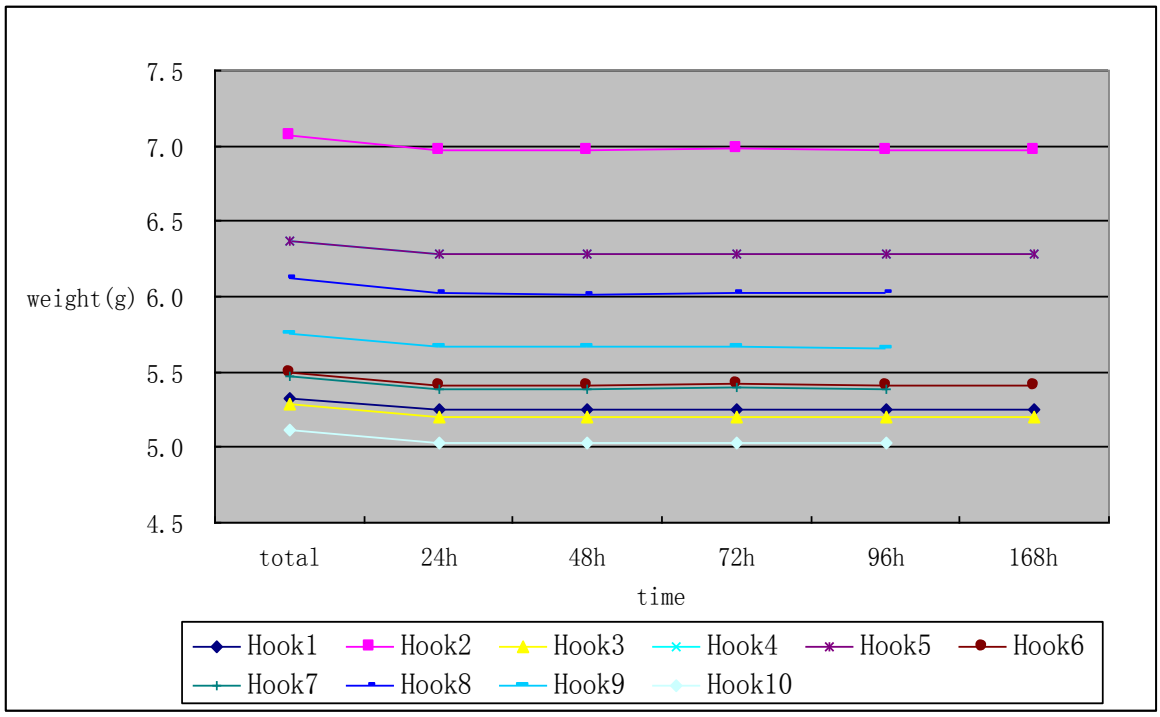


Figure 3.2.1.3.1 Determination of calcium carbonate content of soil-samples from Hook Village by measurement of weight loss from soil at 950 °C

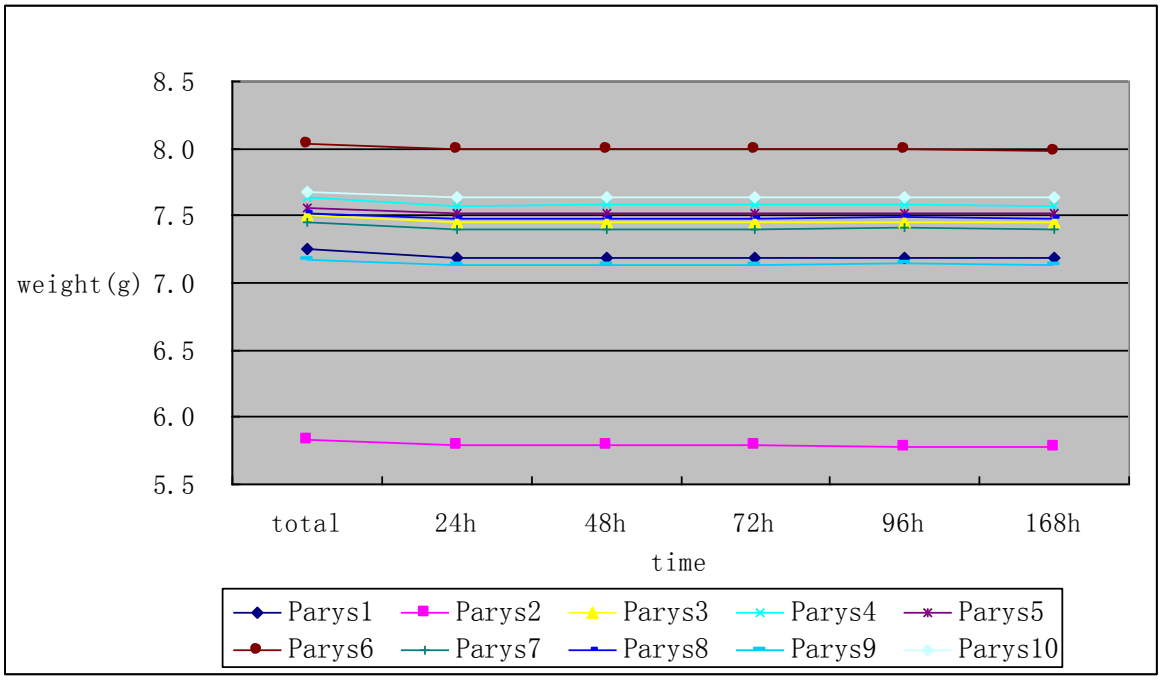


Figure 3.2.1.3.2 Determination of calcium carbonate content of soil-samples from Parys Mountain by measurement of weight loss from soil at 950 °C

Table 3.2.1.3 Calcium carbonate content of soil samples in Hook Village and Parys Mountain

Hook Village			Parys Mountain		
Sample name	mass loss after heating 96 hours (%)	Calcium carbonate content (%)	Sample name	mass loss after heating 96 hours (%)	Calcium carbonate content (%)
Hook e 1	1.30 %	2.96 %	Parys 1	1.00 %	2.27 %
Hook 2	1.29 %	2.94 %	Parys 2	0.90 %	2.05 %
Hook 3	1.6 %	3.72 %	Parys 3	0.68 %	1.54 %

Hook 4	1.28 %	2.91 %	Parys 4	0.73 %	1.66 %
Hook 5	1.31 %	2.97 %	Parys 5	0.50 %	1.15 %
Hook 6	1.54 %	3.49 %	Parys 6	0.63 %	1.42 %
Hook 7	1.55 %	3.51 %	Parys 7	0.60 %	1.35 %
Hook 8	1.60 %	3.64 %	Parys 8	0.48 %	1.10 %
Hook 9	1.79 %	4.07 %	Parys 9	0.55 %	1.25 %
Hook 10	1.70 %	3.85 %	Parys 10	0.59 %	1.35 %
Average	1.50 %	3.41 %	Average	0.67 %	1.52%

From the chart it is clear that the mass of the samples changes very little upon heating for more than 24 hours. Some data points are missing as the Hook samples 7-10 were heated for 96 hours with no further measurements. This was due to a Bank Holiday closure of the laboratory. The amounts of calcium carbonate in all samples were calculated by mass loss after heating for 96 hours.

Initially all the soil samples were heated at 105 °C to remove water content and heated at 450 °C to remove organic content. They were then heated to 950 °C to measure the $CaCO_3$ content [14, 15]. The average is as follows:

Hook Village: 3.41 % ± 0.43 % of the sample is calcium carbonate.

Parys Mountain: 1.52 % ± 0.38 % of the sample is calcium carbonate.

From step 3.2.1.2, dry sample of Hook Village has 9.07 % ± 0.17 % of organic matter and dry sample of Parys Mountain has 4.41 % ± 0.38 % organic matter. So the following calcium carbonate content of each dry sample was determined. The average is as follows:

Hook Village: 3.10 % ± 0. 43 % of the sample is calcium carbonate.

Parys Mountain: 1.45 % ± 0.38 % of the sample is calcium carbonate.

As dolomite is also a common carbonate mineral, magnesium carbonate may appear in soil samples. When the heating temperature is more than 500 °C, magnesium carbonate can decompose to magnesium oxide [16]. Thus the mass loss on heating may be not only from calcium carbonate but also from magnesium carbonate. The relevant equation is:

$MgCO_3$ (s) → MgO (s) + CO_2 (g).

Thus for every mole of $MgCO_3$ (ca. 84 g) one mole of CO_2 (ca. 44 g) is lost.

If it is assumed that the carbonate content is all from magnesium carbonate, the thermal gravimetric analysis results shown in Table 3.2.1.4 would be calculated.

Table 3.2.1.4 Magnesium carbonate content of soil samples in Hook Village and Parys Mountain

Hook Village			Parys Mountain		
Sample name	mass loss after heating 96 hours (%)	Magnesium carbonate content (%)	Sample name	mass loss after heating 96 hours (%)	Magnesium carbonate content (%)

Hook 1	1.30 %	2.48 %	Parys 1	1.00 %	1.90 %
Hook 2	1.29 %	2.47 %	Parys 2	0.90 %	1.72 %
Hook 3	1.6 %	3.13 %	Parys 3	0.68 %	1.30 %
Hook 4	1.28 %	2.45 %	Parys 4	0.73 %	1.39 %
Hook 5	1.31 %	2.49 %	Parys 5	0.50 %	0.96 %
Hook 6	1.54 %	2.93 %	Parys 6	0.63 %	1.20 %
Hook 7	1.55 %	2.95%	Parys 7	0.60 %	1.14 %
Hook 8	1.60 %	3.05 %	Parys 8	0.48 %	0.92 %
Hook 9	1.79 %	3.42 %	Parys 9	0.55 %	1.05 %
Hook 10	1.70 %	3.24 %	Parys 10	0.59 %	1.14 %
Average	**1.50 %**	**2.86 %**	**Average**	**0.67 %**	**1.27%**

Hook Village: 2.86 % ± 0.36 % of the sample is magnesium carbonate.

Parys Mountain: 1.27 % ± 0.32 % of the sample is magnesium carbonate.

From step 3.2.1.2, dry sample of Hook Village has 9.07 % ± 0.17 % of organic matter and dry sample of Parys Mountain has 4.41 % ± 0.38 % organic matter. So the following calcium carbonate content of each dry sample was determined. The average is as follows:

Hook Village: 2.60 % ± 0. 36 % of the sample is magnesium carbonate.

Parys Mountain: 1.21 % ± 0.32 % of the sample is magnesium carbonate.

In fact the carbonate content of these samples will be a mixture of calcium and magnesium carbonates so the actual carbonate content will be somewhere between the values calculated for pure $CaCO_3$ and pure $MgCO_3$.

3.2.2 pH measurement

The table 3.2 shows the pH value of suspensions formed by mixing different amounts of soil samples (0.5 g and 2 g) from Hook Village and Parys Mountain with 20 mL of deionised water.

Table 3.2 pH values obtained for different amount of soil samples from two different sites mixed with 20 ml deionised water respectively

pH value of Hook Village			pH value of Parys Mountain		
Soil	0.5 g	2 g	Soil	0.5 g	2 g
sample 1	6.12	5.17	sample 1	7.33	7.38
sample 2	6.16	5.14	sample 2	7.39	7.18
sample 3	6.16	5.08	sample 3	7.46	7.14

sample 4	6.04	5.32	sample 4	7.43	7.24
Average	**6.12 ± 0.06**	**5.18 ± 0.10**	**Average**	**7.40 ± 0.06**	**7.24 ± 0.11**

From the table, it is clear that when using 0.5 g soil mixed with deionised water, the pH value for Hook Village samples was 6.12 ± 0.06 and the pH value for Parys Mountain was 7.40 ± 0.06. When using 2 g soil mixed with deionised water, the pH value for Hook Village samples was 5.18 ± 0.10 and the pH value for Parys Mountain was 7.24 ± 0.11. It is shown that the pH value changed as different amounts of soil were used. But from both results, the most notable observation is that the Hook Village samples are mildly acidic and the Parys Mountain samples are slightly alkaline. As the pH value of deionised water is 7.00, when more acidic soil from Hook Village was added into the deionised water, the mixed solution became more acidic. But when different amounts of soil from Parys Mountain were added into deionised water, the pH value did not increase as expected. One possibility is the mixed solution from Parys Mountain acts as a buffer solution.

Comparing the results from thermal analysis, in chapter 3.2.1, Hook Village has more calcium carbonate content (3.10 % ± 0. 43 %) than Parys Mountain (1.45 % ± 0.38 %) and the amount of organic content of Hook Village (9.07 % ± 0.17 %) is also bigger than Parys Mountain (4.41% ± 0.38 %). Calcium carbonate can make the mixed solution more alkaline, but more organic content may make the solution more acid. As calcium carbonate is sparingly soluble in water (15 mg / L at 25 °C) [16], the organic content may have more effect on the pH value of the soil samples.

It is known that pH will affect the leaching of metals from soil samples with metals generally being more mobile at low pH [17]. This point will be investigated further when leaching experiments are performed.

3.2.3 Infrared Spectroscopy

Infrared Spectroscopy was used to identify some of the minerals present in the samples [18]. As soil samples are always non-homogeneous, four samples have been chosen from each site. Here just two figures of soil samples from Hook Village and one figure of soil sample from Parys Mountain showing typical infrared spectra are given but full details and spectra can be seen in the Appendix.

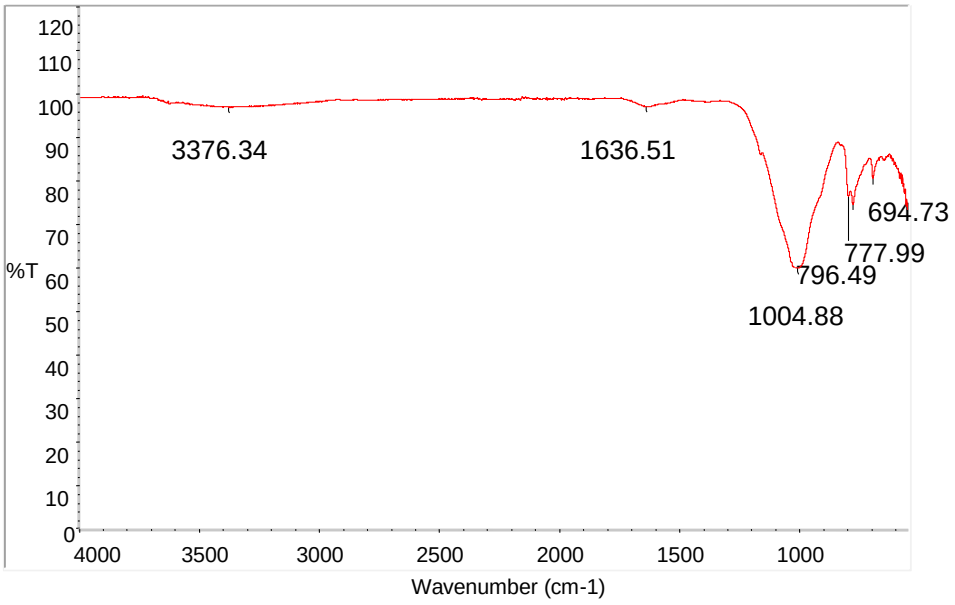


Figure 3.2.3.1 Infrared spectrum of dried soil sample 2 from Hook Village

From the figure above, the small peaks at 3200-3400 cm^{-1} and 1600-1700 cm^{-1} may come from H_2O as the stretching and bending modes of the OH bonds respectively. This may indicate that the sample is a little damp even after drying as a result of taking up moisture

from the atmosphere. Alternatively these peaks could come from water molecules trapped within the structure of clay minerals. The peak at 1000 - 1100 cm^{-1} is almost certainly from the υ (Si-O) stretching vibration and comes from quartz, silicates or clay minerals [19, 20, 21]. Quartz is one of the most common minerals in the Earth's crust which is a crystalline form of silica (SiO_2) [22]. The absorption band at 778 cm^{-1} may be δ (Si-O) and probably comes from Quartz. The peak at 797 cm^{-1} indicates that amorphous silica is also present [23, 24]. The peak at 690 cm^{-1} may be an O- Si-O bend.

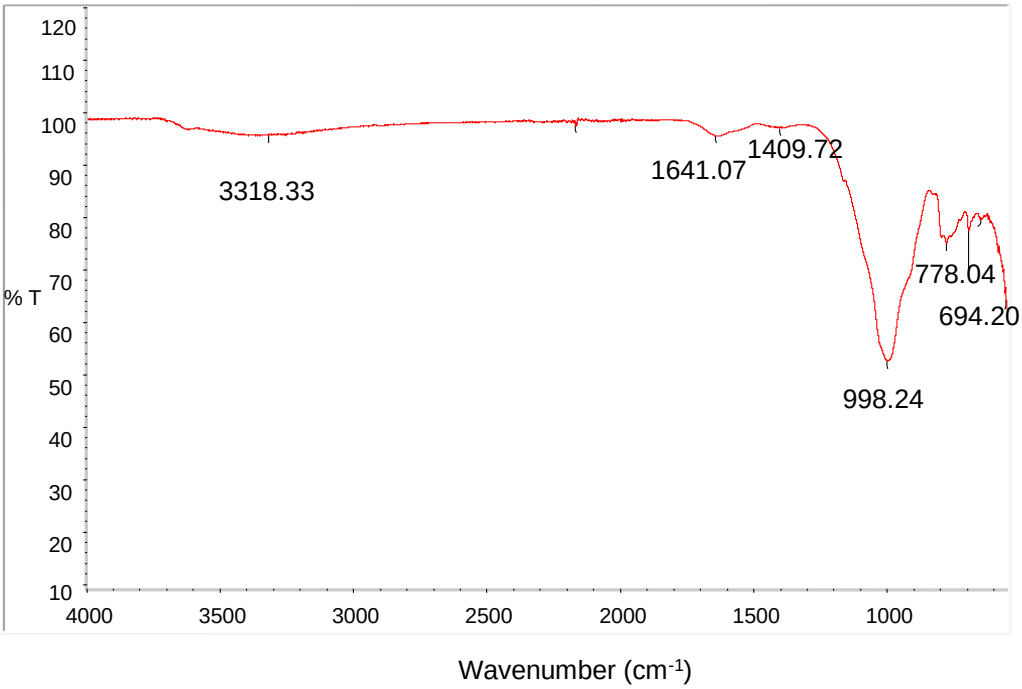


Figure 3.2.3.2 Infrared spectrum of dried soil sample 1 from Hook Village

From figure 3.2.3.2, a small peak at 1409 cm^{-1} may be from the CO_3^{2-} asymmetric stretch vibration. It arises from carbonate minerals such as calcite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) [22]. This backs up the results of thermal analysis that Hook Village has nearly 3.10 % calcium carbonate content or nearly 2.6 % magnesium carbonate. As soil

samples are never homogenous and IR experiments only use very small amount of soil samples, not every repeat experiment may show a carbonate peak in the infrared spectrum as not every sample may contain enough carbonate for the peak to be visible.

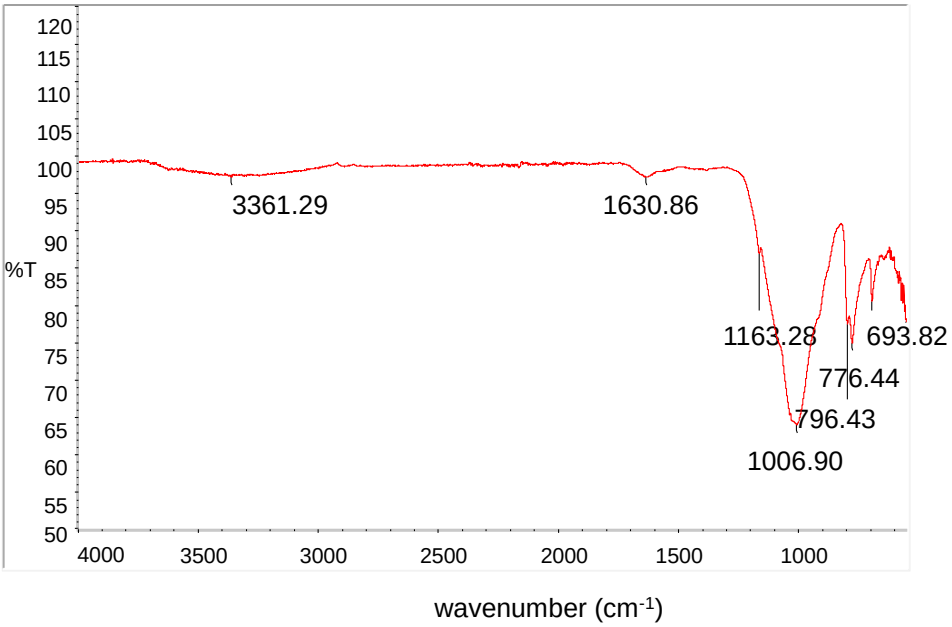


Figure 3.2.3.3 Infrared spectrum of dried soil sample 3 from Parys Mountain

From the figure above, the small peaks at 3200-3400 cm^{-1} and 1600-1700 cm^{-1} are from water. The small peak at a wavenumber between 1040-1210 cm^{-1} may be the $\upsilon(SO_4^{2-})$ asymmetric stretching vibration of the sulfate ion and may come from a sulfate mineral such as barite ($BaSO_4$) or gypsum ($CaSO_4$). The peak at 1000 - 1100 cm^{-1} may be υ(Si-O) and come from quartz, silicates or a clay mineral. The absorption band at 1007 may be υ(Si-O-Al) from some common clay minerals such as kaolinite ($Al_2(OH)_4Si_2O_5$) or montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$) [25, 26]. The peak at 778 cm^{-1} may be δ(Si-O) and come from quartz. The peak at 693 cm^{-1} may be an O- Si-O bend.

From the three figures, the most important specific observations from the infrared spectra

are as follows:

1. Quartz is present in all samples, clearly identified by the sharp doublet at 778 cm^{-1} and 797 cm^{-1}.

2 Clay minerals may be present in both samples identified by υ(Si-O) at 1000-1100 cm^{-1}.

3. A sulfate-containing mineral, probably barite ($BaSO_4$) or gypsum ($CaSO_4$) is present in the Parys Mountain soil as there are some peaks between 1040-1210 cm^{-1} which come from υ(SO_4^{2-}) stretching vibration.

4. There is evidence of $CaCO_3$ or $MgCO_3$ in the samples studied here which is characterized by a band around 1409 cm^{-1} from the asymmetric stretching of the carbonate ion.

3.2.4 X-ray Fluorescence Spectroscopy

X-ray Fluorescence spectroscopy (XRF) results can show which specific metals contaminate the soils and the concentrations of these metals [7]. It can give some suggestion of which elements should be selected to study in leaching experiments and can give an amount of each element in the samples. The two tables 3.2.4.1 and 3.2.4.2 show the percentage and concentrations of elements in the soil samples which were detected by XRF.

Table 3.2.4.1 Percentages of elements of soil samples from Hook Village and Parys Mountain determined by X-ray Fluorescence

Elements	Percentages of elements from Hook Village (%)	Percentages of elements from Parys Mountain (%)
Si	32.25±0.17	39.15±1.04
Al	7.56±0.06	2.42±0.12
Fe	4.69±0.11	2.56±0.03
K	1.80±0.01	0.96±0.04
Mg	0.72±0.01	0.21±0.02
Na	0.71±0.02	0.06±0.01
Ti	0.51±0.00	0.18±0.01
Ca	0.25±0.00	0.41±0.03
P	0.22±0.01	0.12±0.01
Mn	0.19±0.00	0.05±0.00

Table 3.2.4.2 Concentrations of elements of soil samples from Hook Village and Parys Mountain determined by X-ray Fluorescence

Elements	Concentrations of elements from Hook Village (ppm)	Concentrations of elements from Parys Mountain (ppm)
Pb	**379±6.1**	**264±25.5**
Zn	**309±4.2**	**103±3.2**
Zr	276±3.5	267±23.8
Cu	**225±2.2**	**96±5.9**
V	116±4.6	27±6.8
Rb	112±1.0	50±1.5
Cr	81±2.8	39±3.6
Sr	58±0.5	37±1.3
Y	31±0.8	15±0.6
Ni	24±1.4	12±0.0
Co	19±1.0	9±0.6

(1 % = 10^4 mg / kg = 10^4 ppm)

The results show that the two sites are particularly high in iron. Iron, after oxygen, silicon and aluminum, is the fourth most abundant element in the earth's crust. Iron is an

interesting metal to study in leaching experiments as alongside its solubility in various media iron shows oxidation states of +Ⅱ and +Ⅲ so redox chemistry may also occur. Interestingly the levels of copper from the Parys Mountain site (known to be a major copper-mining area) are not particularly high (95.8 ppm) but it is still nearly four times higher than mean value for the whole of Wales (23.23 ppm) [27].

The amounts of calcium and magnesium in both sites are not too high and these results can be compared with the results of heating soil samples at 950 °C (in chapter 3.2.1.3) to determinate the carbonate content of soil samples. However, the calcium content of the Hook Village samples is lower (0.25 %) than that of the Parys Mountain samples (0.41%) which is different from the results of heating calcium carbonate from samples (assuming the carbonate content comes from calcium carbonate, Hook Village: 3.10 % calcium carbonate which would indicate 1.24 % Ca, Parys Mountain: 1.45 % calcium carbonate which would indicate 0.58 % Ca). One reason for this discrepancy in Ca concentration may be because some Ca is present as $CaSO_4$ in the Parys Mountain samples. This again backs up the results of IR spectroscopy that there is a peak at wavenumber 1160 cm^{-1} may be the $\upsilon(SO_4^{2-})$ and come from sulfate mineral. Another reason may be that some of the carbonate content not only includes calcium carbonate but also includes magnesium carbonate. The amount of magnesium determined by XRF in the Hook Village sample (0.72 %) is higher than that in the Parys Mountain sample (0.21%). If it were assumed that all of the Mg is present as $MgCO_3$ then these Mg concentrations would equate to 2.52 % $MgCO_3$ (Hook Village) and 0.74 % $MgCO_3$ (Parys Mountain). These values suggest that a significant amount of the carbonate in these soil samples may be present as $MgCO_3$. Magnesium is one of the most common metals in nature and the percentage of magnesium in earth crust is about 2.4 % [16]. The principal minerals are dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), carnallite $KCl•MgCl_2•6H_2O$, and silicate materials. Lastly these results also show that all of the soils contain high levels of silicates as the percentage of Si is very high (Hook Village: 32.25 %, Parys Mountain: 39.15 %). This backs up the results of IR spectroscopy.

From the report of UK soil and Herbage pollutant Survey report No. 7 from The

Environment agency [27], concentrations of copper, zinc and lead in rural soils of Wales have mean values of 23.23 ppm, 87.9 ppm and 59.2 ppm, respectively. The average concentration of iron, copper, zinc and lead of Hook Village and Parys Mountain are shown in table 3.2.4.3. Both sites contained high levels of Cu, Zn and Pb. Partly on the basis of elemental analysis by X-ray Fluorescence, copper, zinc, iron and lead were selected as representative metals to study in leaching experiments.

Table 3.2.4.3 Average concentration of four metals (Fe, Cu, Zn and Pb) in soil samples from Hook Village and in Parys Mountain determined by XRF

	Fe	Cu	Zn	Pb
Hook Village	4.69 ± 0.11%	225 ±2.2 ppm	309 ±4.2 ppm	379 ±6.1 ppm
Parys Mountain	2.56 ± 0.03 %	96 ±5.9 ppm	103 ±3.2 ppm	264 ±25.5 ppm

3.2.5 Atomic Absorption Spectroscopy

Leaching experiments have played a central role in this research. In this chapter, atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) were used to analyse leachate solutions [7]. The leaching results were affected by the acidity of the matrices (details can be seen in chapter 4) and they were also affected by the presence of anions which may influence the solubility of the metal ions e.g. SO_4^{2-} and Cl^- in sulfuric and hydrochloric acid. Here four different solutions (0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, 0.1 M EDTA-2Na,) were selected as matrices.

Ethylenediaminetetraacetic acid, widely abbreviated as EDTA, is a colorless solid. EDTA

is one of the most popular and efficient chelating agents to increase the solubility of metals in soil [28] and has been widely used for the extraction of heavy metals from contaminated soils [29, 30, 31, 32]. As the solubility of EDTA is quite low, for leaching experiments, EDTA salts were widely used. In this chapter, EDTA-2Na was used to prepare EDTA solution. The further study using EDTA salts solution as matrices can be seen in Chapter 5.

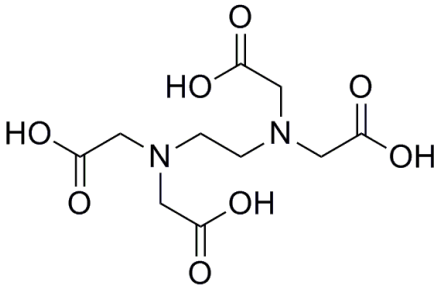


Figure 3.2.5.1 the Structure of EDTA

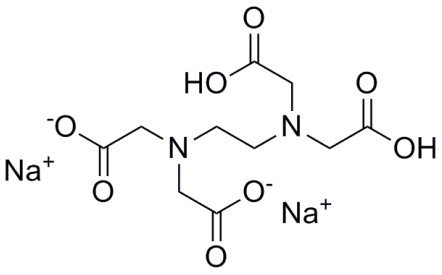


Figure 3.2.5.2 the structure of EDTA-2Na

The following figures show the concentrations of Cu, Pb, Zn and Fe obtained in leaching experiments when using different solutions as matrices and as detected by AAS. The leaching results detected by AAS were also compared with those detected by ICP-MS in chapter 3.2.6.

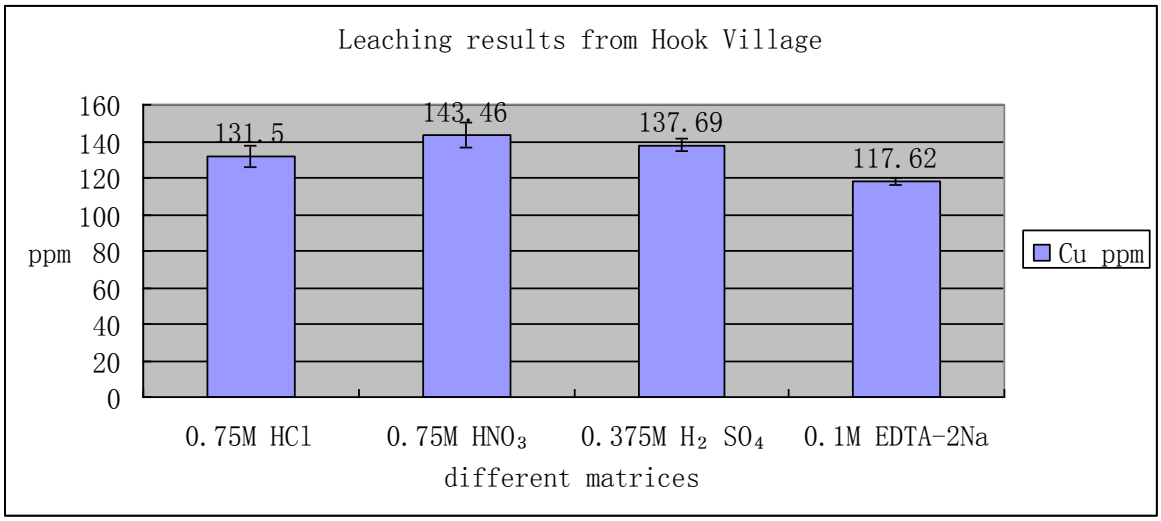


Figure 3.2.5.3 A graph showing the concentrations of Cu leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

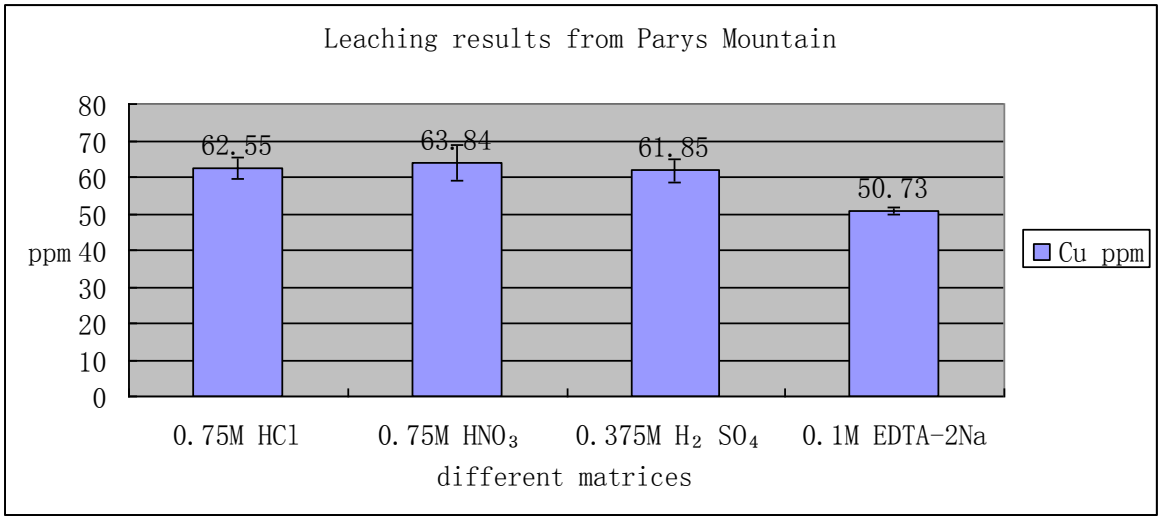


Figure 3.2.5.4 A graph showing the concentrations of Cu leached from Parys Mountain using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

From Figure 3.2.5.3 and Figure 3.2.5.4 above, the three strong acids (HCl, HNO_3 and H_2SO_4) (which have similar pH values as they are fully ionized) give similar

concentrations of copper in the leachates. EDTA-2Na solution is generally a poorer leachate than hydrochloric, nitric or sulfuric acids for leaching Cu from the soil samples. The error bars in both figures show the standard deviation of each result as all the samples had four repeat experiments and here is shown the average of the results.

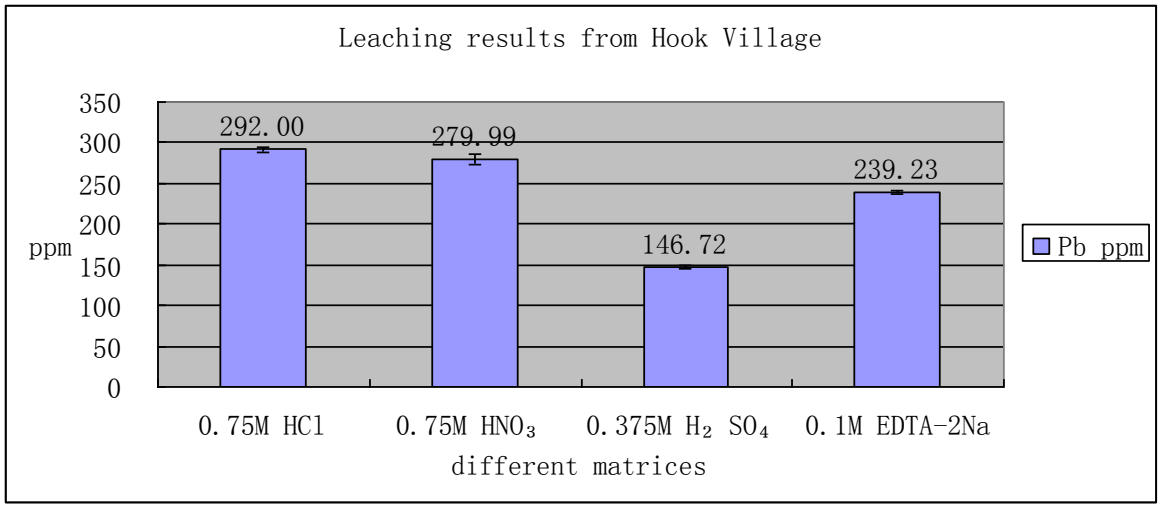


Figure 3.2.5.5 A graph showing the concentrations of Pb leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

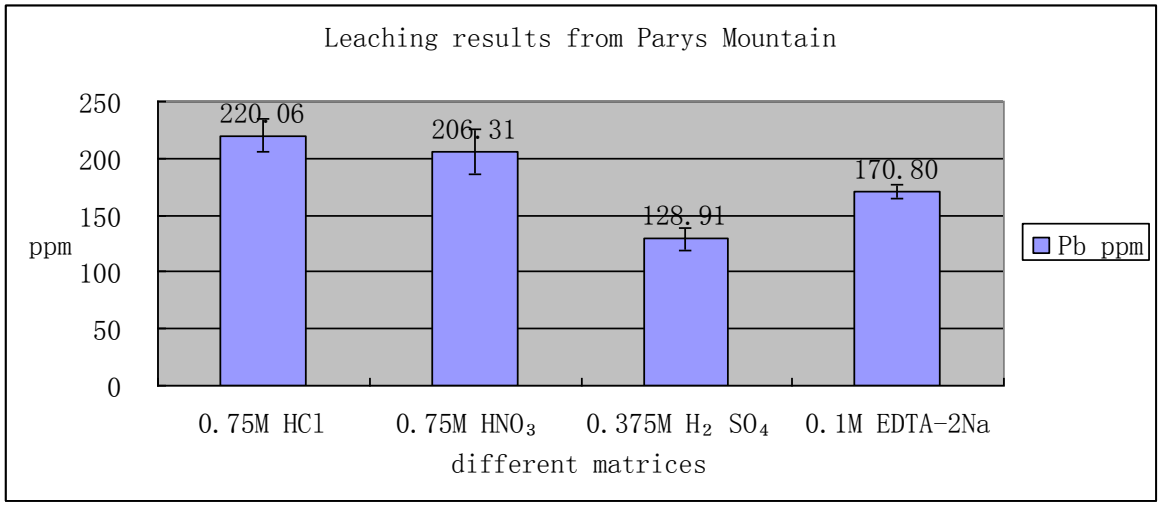


Figure 3.2.5.6 A graph showing the concentrations of Pb leached from Parys Mountain using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

From Figure 3.2.5.5 and Figure 3.2.5.6 above, it is shown that EDTA-2Na solution is generally a poorer leachate than hydrochloric acid and nitric acid for leaching Pb from the soil samples. But EDTA-2Na solution leached more Pb than did sulfuric acid. There is a clear difference between sulfuric acid and hydrochloric acid as leachates. Sulfuric acid only leached 50 % of the amount of lead that hydrochloric acid leached (HCl: 292 ppm, H_2SO_4: 147ppm) from Hook Village and 59 % (HCl: 220 ppm, H_2SO_4: 129ppm) from Parys Mountain. The reason may be because lead sulfate ($PbSO_4$) is very slightly soluble in water (42.5 mg / L at 25 °C) while lead chloride ($PbCl_2$) is much more soluble (9.9 g / L at 25 °C). Thus in water the limit of solubility of $PbSO_4$ would be expected to be around 42.5 ppm. This figure suggests that it is indeed the solubility of $PbSO_4$ which is limiting the amount of Pb that can be leached in H_2SO_4. And in diluted acid, the solubility of $PbSO_4$ has a small increase. The relevant equations are:

$H_2SO_4(aq) \leftrightharpoons HSO_4^-(aq) + H^+(aq)$,

$HSO_4^-(aq) \leftrightharpoons SO4^{2-}(aq) + H^+(aq)$,

$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

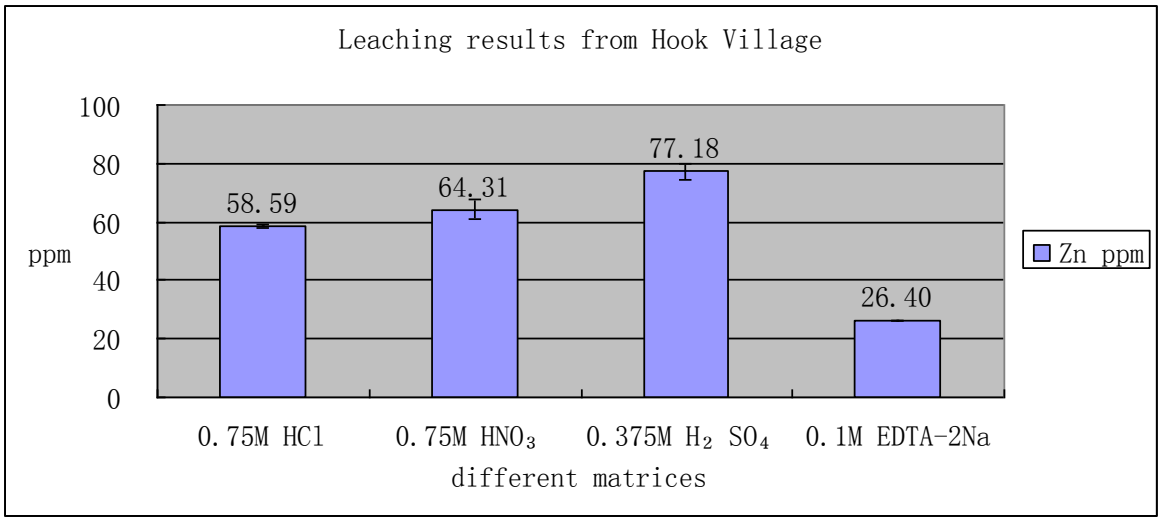


Figure 3.2.5.7 A graph showing the concentrations of Zn leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

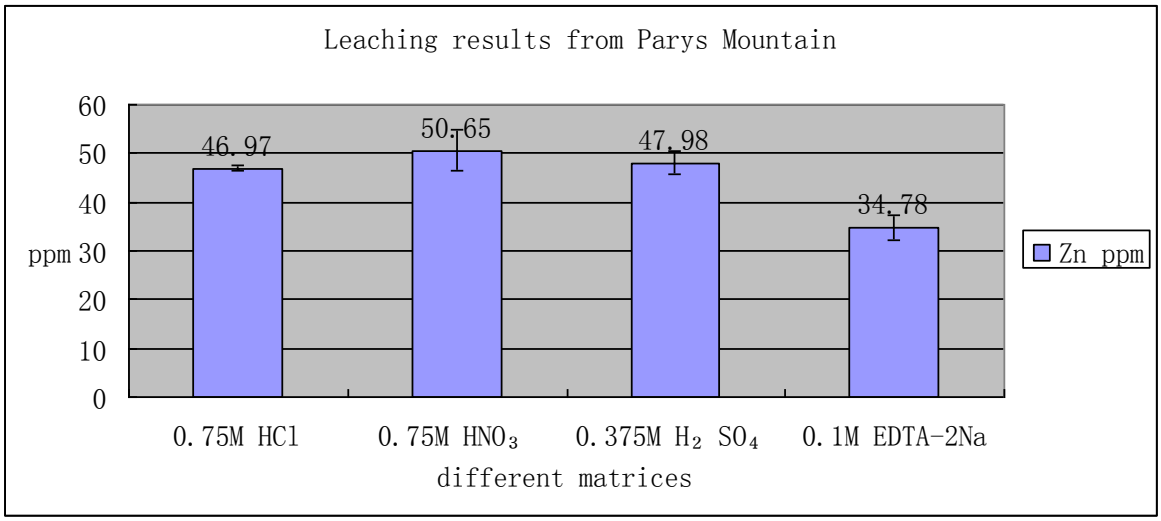


Figure 3.2.5.8 A graph showing the concentrations of Zn leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

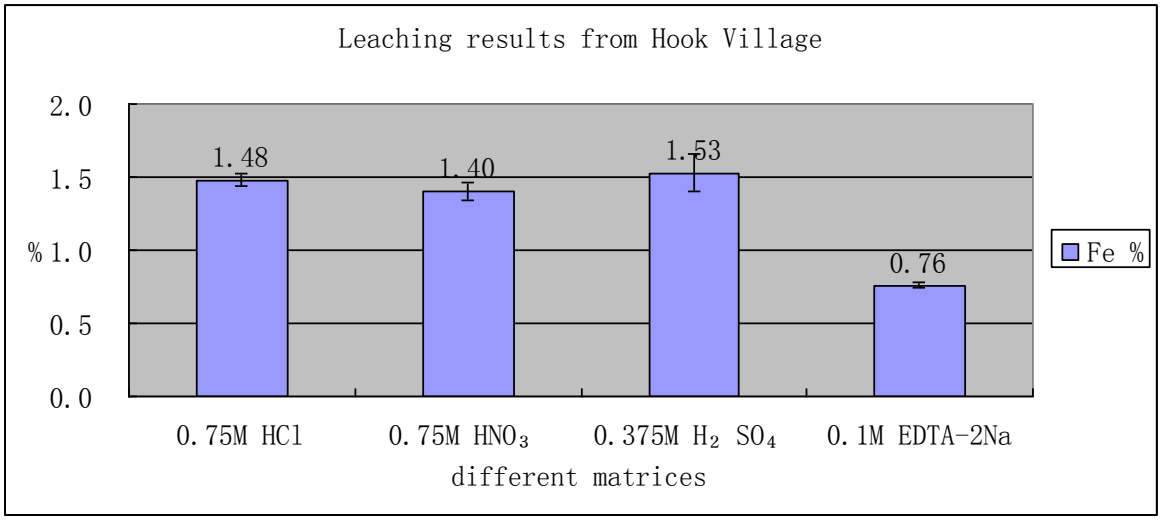


Figure 3.2.5.9 A graph showing the concentrations of Fe leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

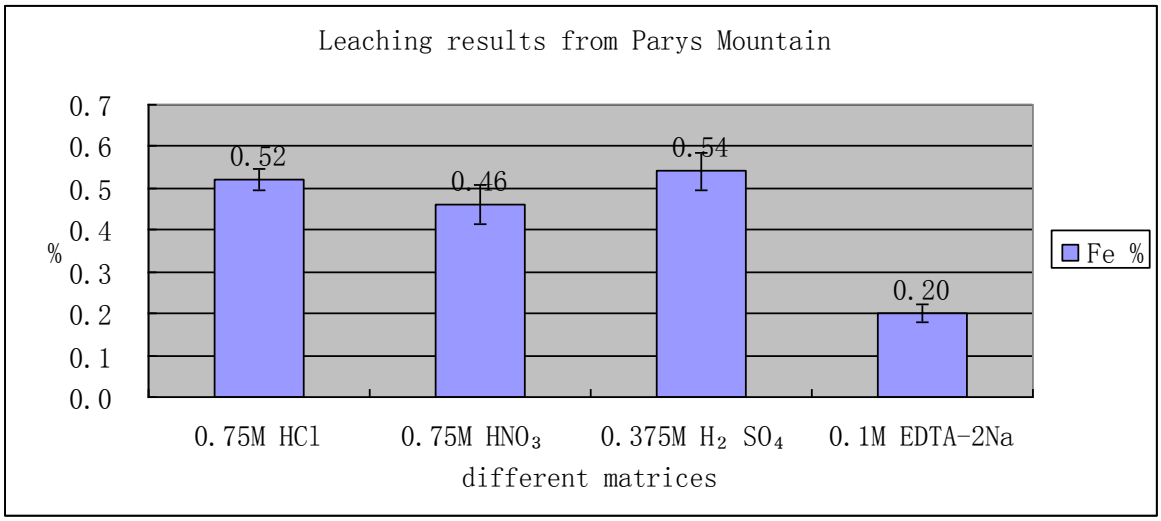


Figure 3.2.5.10 A graph showing the concentrations of Fe leached from Parys Mountain using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and 0.1 M EDTA-2Na as matrices by AAS

From the four Figures above, EDTA-2Na solution is seen to be a much poorer leachate than the other three acids for leaching both Zn and Fe. The four matrices can remove Pb, Zn, Cu and Fe from soil samples from both Hook Village and Parys Mountain but have different efficiencies. A further study of using different concentrations of the three acids to find which concentration was most efficient for leaching metals from soil has been carried out in Chapter 4.

3.2.6 Inductively coupled plasma mass spectrometry

In this research, a Thermo Scientific™ iCAP™ Q ICP-MS instrument and ASX-520 autosampler instrument were used to analyse simultaneously ten different heavy metals (V, Cr, Co, Ni, Cu, Zn, Sr, Zr, Pb and Fe) leached from the samples at room temperature.

ICP is used routinely to determine ppb and ppm concentrations of most metal elements. All

the leachates were diluted 100 times using 2 % HNO_3 solution with 5 ppb Rh added as an internal calibrant. As iron has a particularly high concentration in the soil samples studied, the leachates had to be diluted 5000 times to be run in the instrument to determine the iron concentration. Thus the results for iron were less precise and accurate after so much dilution. Thus, in the table 3.2.6 below are only shown the concentrations of other nine elements (V, Cr, Co, Ni, Cu, Zn, Sr, Pb and Zr).

Table 3.2.6 Concentrations of nine elements (V, Cr, Co, Ni, Cu, Zn, Sr, Pb and Zr) of soil samples from Hook Village and Parys Mountain leached by different matrices (0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, 0.1 M EDTA-2Na) and determined by ICP

	^{51}V	^{52}Cr	^{59}Co	^{60}Ni	^{63}Cu	^{66}Zn	^{88}Sr	^{208}Pb	^{90}Zr
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
HookVillage-HNO_3	22.51	16.51	6.59	8.74	167.51	65.53	8.75	274.16	5.34
HookVillage-HCl	24.88	11.89	8.47	8.51	166.54	67.84	10.59	301.69	6.62
HookVillage-H_2SO_4	25.15	14.01	6.8	10.16	184.87	73.61	5.89	153.52	-
HookVillage-EDTA-2Na	14.36	6.15	4.03	3.12	180.33	30.63	6.4	237.98	4.88
Parys Mountain-HNO_3	13.03	10.26	2.54	18.73	75.56	51.56	13.55	197.2	0.73
Parys Mountain-HCl	12.76	24.68	2.16	9.57	63.46	46.79	11.35	218.38	-
Parys Mountain-H_2SO_4	13.41	8.96	2.41	9.85	87.57	46.55	11.9	128.15	-
Parys Mountain-EDTA-2Na	8.36	3.96	1.52	6.14	59.42	30.34	10.18	158.46	5.22

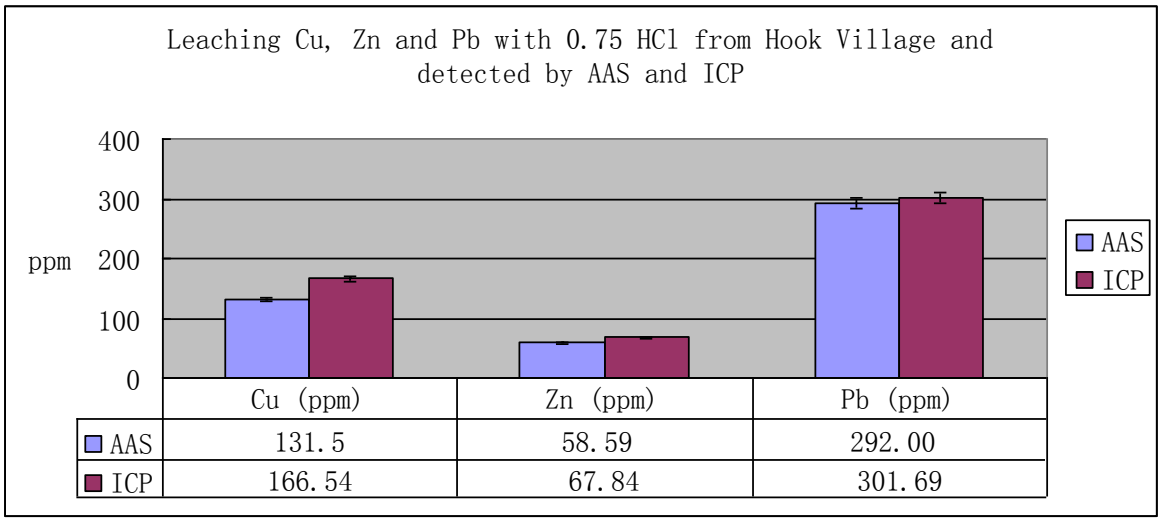
Comparing the results with those in Table 3.2.6 and Table 3.2.4.2, it shows that the four matrices employed successfully leached all eight elements from soil samples from both Hook Village and Parys Mountain. For Zr, the concentration of Zr in Hook Village is nearly 276 ppm while in Parys Mountain is 267 ppm. Zirconium is found in small amounts widely spread throughout nature and the abundance of zirconium in the Earth's crust is estimated as 165 ppm [16]. The most common zirconium-containing minerals are zircon, or zircon orthosilicate ($ZrSiO_4$). Other zirconium minerals are eudialite (Na, Ca, $Fe)_6ZrSi_6O_{18}$(OH, Cl), and baddeleyite (ZrO_2). From the leaching results of ICP-MS, it is clear that sulfuric acid cannot leach out any Zr from the soil samples while the other three matrices only remove small amount of zirconium from the samples. The reason may be that zirconium oxide (ZrO_2) is soluble only in *hot* sulfuric, nitric and hydrochloric acids while zirconium silicate ($ZrSiO_4$) is insoluble in water, acids, aqua regia, and alkalis. The solubility of these minerals probably limited the amount of Zr leached as $Zr(SO_4)_2$ itself is soluble (52.5 g / 100 mL).

Table 3.2.4.2 Concentrations of elements of soil samples from Hook Village and Parys Mountain determined by X-ray Fluorescence

Elements	V	Cr	Co	Ni	Cu	Zn	Sr	Pb	Zr
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Hook Village	115.8	81.3	19.3	24.0	225.0	309.0	58.2	378.5	275.8
Parys Mountain	26.5	38.8	8.5	12.0	95.8	103.0	36.5	263.5	267.3

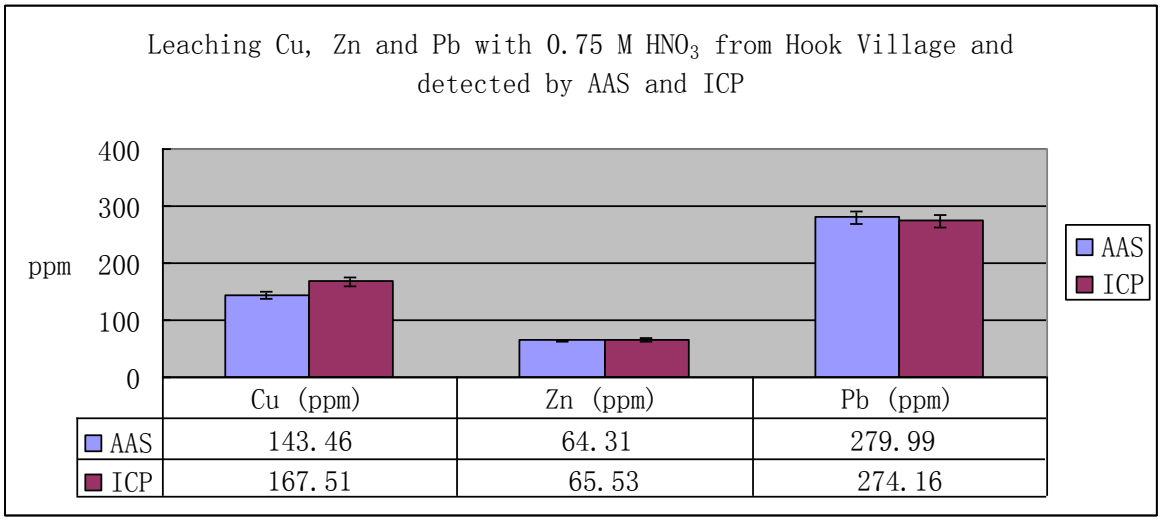
ICP is used routinely to determine ppb and ppm concentrations of most metal elements while AAS determines ppm concentrations of metal elements. The following four figures

show the comparison of the leaching results from Hook Village samples detected by AAS and ICP when using the same matrix.



	Cu (ppm)	Zn (ppm)	Pb (ppm)
AAS	131.5	58.59	292.00
ICP	166.54	67.84	301.69

Figure 3.2.6.1 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.75 M HCl and detected by AAS and ICP



	Cu (ppm)	Zn (ppm)	Pb (ppm)
AAS	143.46	64.31	279.99
ICP	167.51	65.53	274.16

Figure 3.2.6.2 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.75 M HNO_3 and detected by AAS and ICP

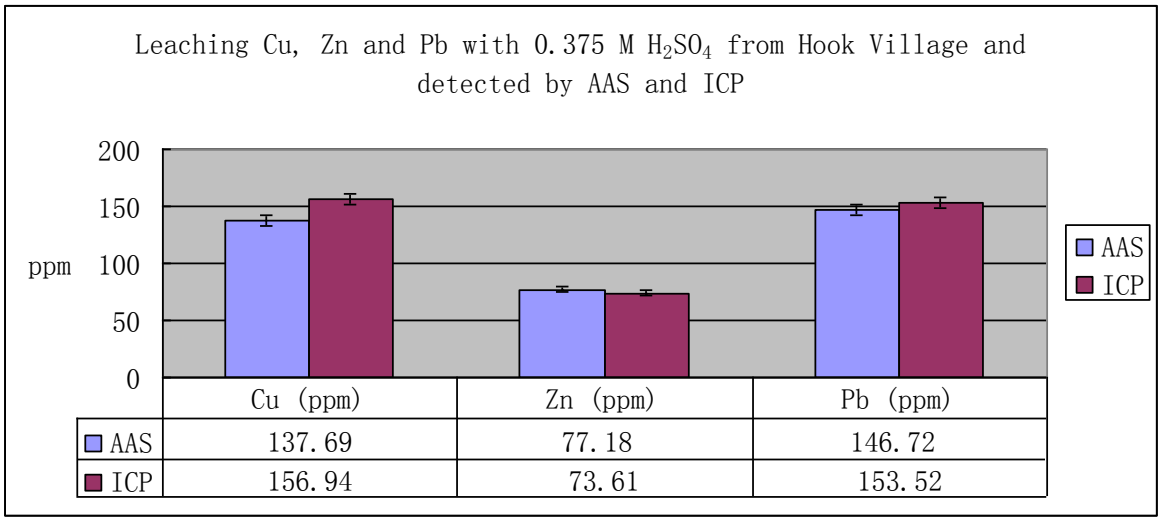


Figure 3.2.6.3 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.375 M H_2SO_4 and detected by AAS and ICP

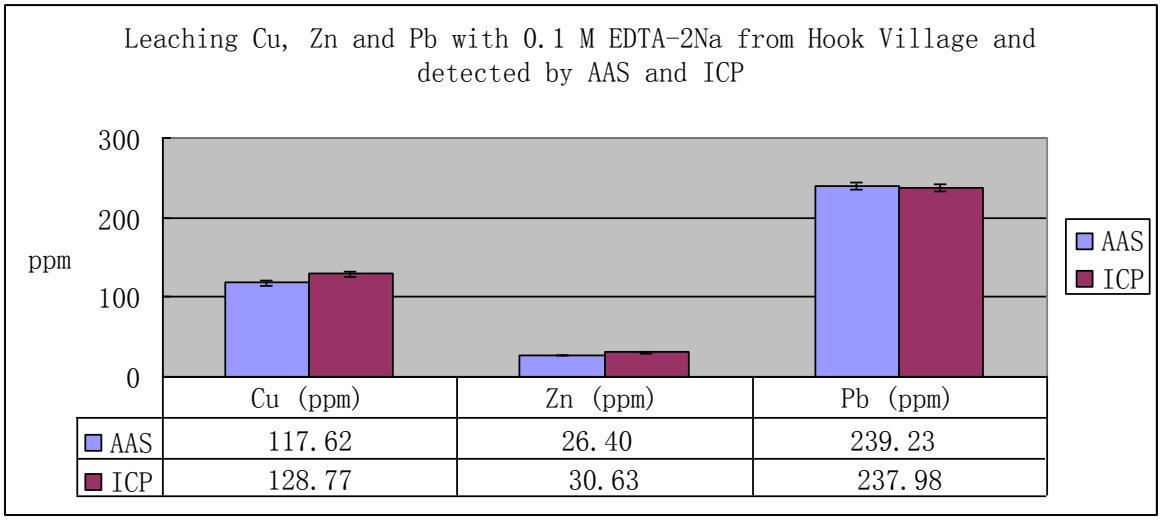
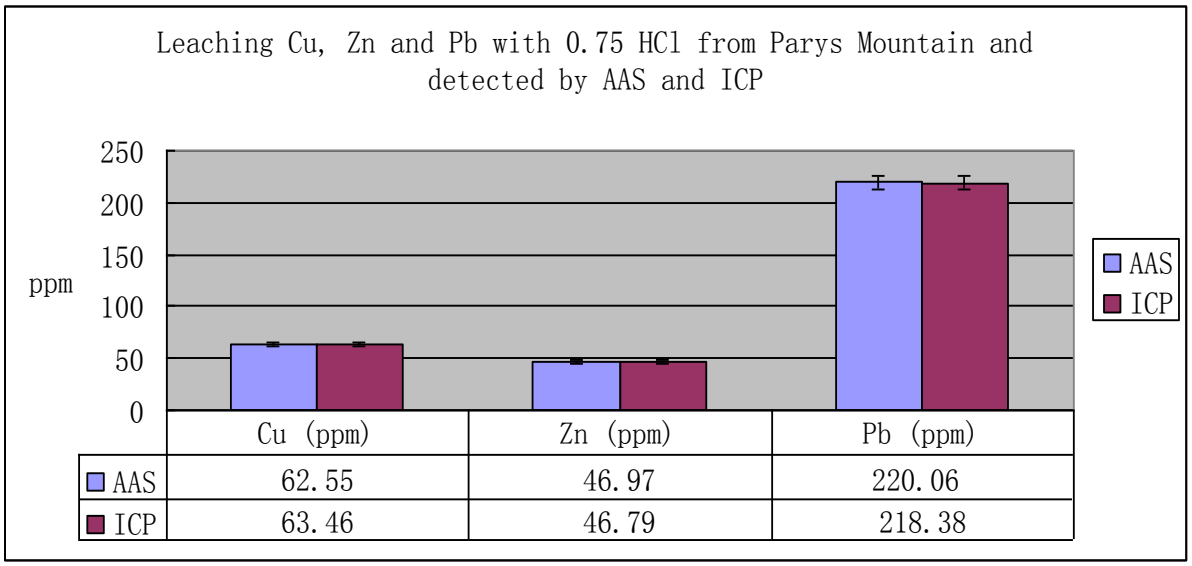


Figure 3.2.6.4 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.1 M EDTA-2Na and detected by AAS and ICP

From Figure 3.2.6.1 to Figure 3.2.6.4, when using four different matrices, the leaching results of the concentrations of Cu, Zn and Pb from Hook Village samples only show small differences even when using different analytical instruments. This means that there is good

correlation between the detection methods of AAS and ICP-MS. One reason for the small differences may be that when the samples are determined by ICP, they need to be diluted 100 times. The large dilution factor may add some errors.

The following four figures show the comparison of the leaching results from Parys Mountain samples detected by AAS and ICP when using the same matrix. They are very comparable to the results from the Hook Village samples.



	Cu (ppm)	Zn (ppm)	Pb (ppm)
AAS	62.55	46.97	220.06
ICP	63.46	46.79	218.38

Figure 3.2.6.5 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.75 M HCl and detected by AAS and ICP

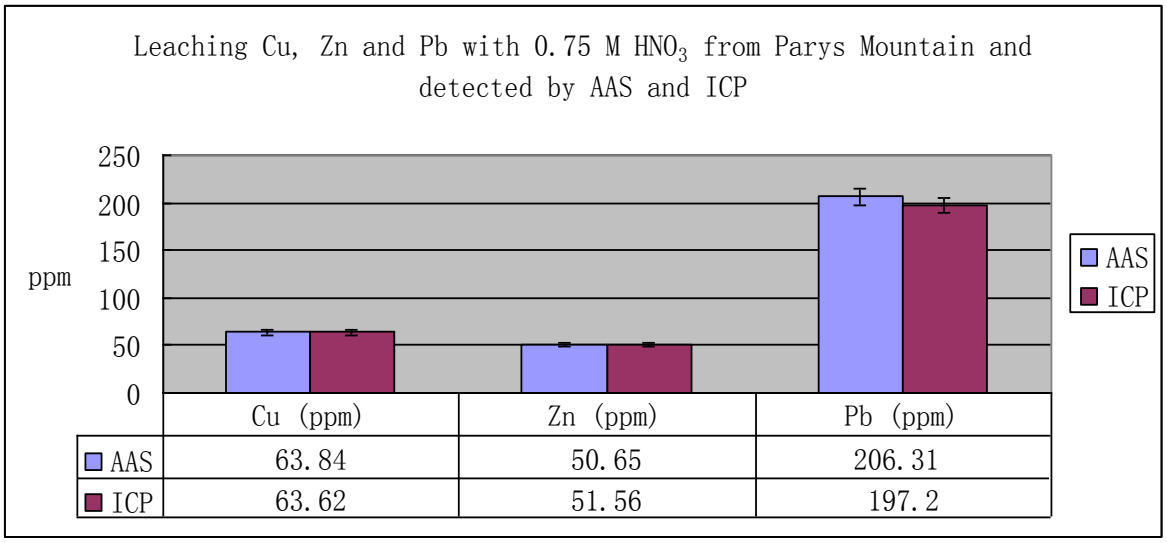


Figure 3.2.6.6 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.75 M HNO_3 and detected by AAS and ICP

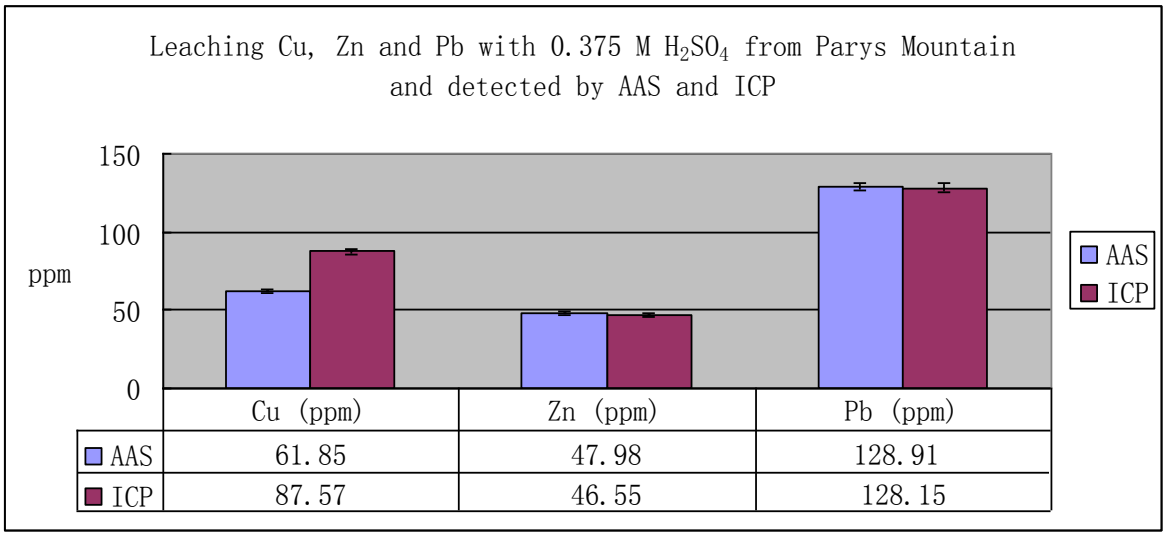


Figure 3.2.6.7 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.375 M H_2SO_4 and detected by AAS and ICP

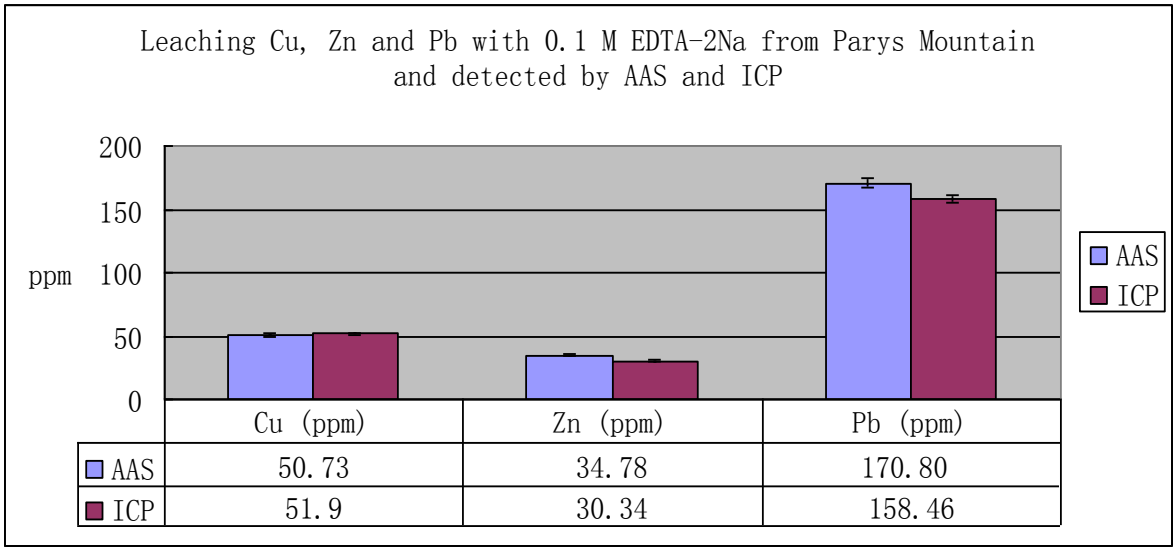


Figure 3.2.6.8 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.1 M EDTA-2Na and detected by AAS and ICP

The leaching results of Cu, Zn and Pb from ICP-MS are generally similar to the results from AAS. This finding also gives confidence in the robustness of the method and the accuracy of the results obtained. They also confirm the conclusions that EDTA is a poorer leachate. But for Pb, sulfuric acid was the poorest leachate. However, there are some differences between the results from AAS and ICP-MS. In Figure 3.2.6.7, when using 0.375 M H_2SO_4 as matrices, the value for Cu determined by AAS is a little lower than the value determined by ICP. As previously mentioned this discrepancy may result from the bigger dilution factor for ICP measurements. Another possible explanation for the discrepancy is post-calibration instrumental drift.

3.2.7 Particle size analysis

Soil contains a wide range of particles with different size fractions. Differently sized

particles have different mobility [33, 34]. In this part, three different diameter size ranges were studied: sand-sized aggregates (63-2000 μm), silt-sized aggregates (2-63μm) and clay (0.01-2μm). Figure 3.2.7.1 shows the particle size distribution for each sample and Figure 3.2.7.2 shows the classification of the soils according to this distribution. The results of mode particle size are tabulated in table 3.2.7.

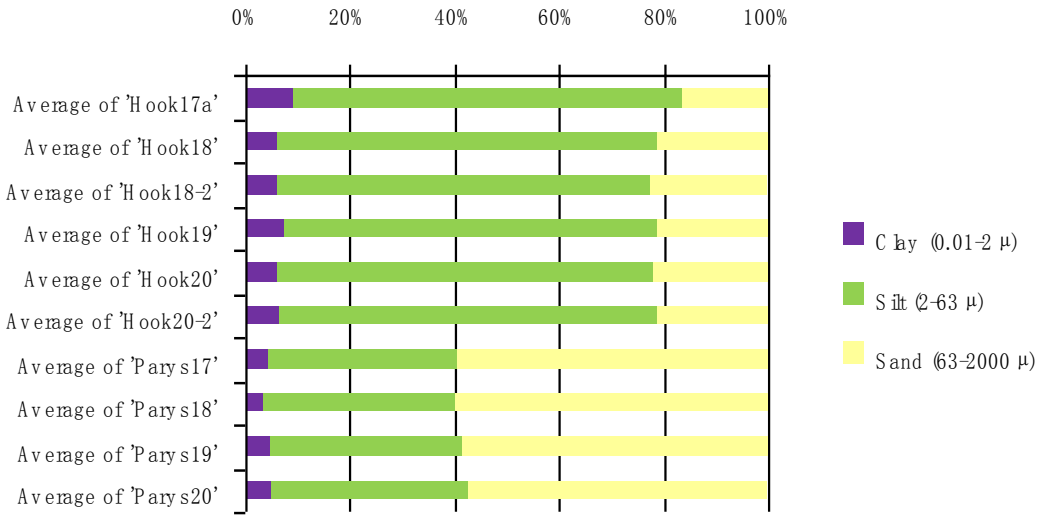


Figure 3.2.7.1 the particle size distribution for each sample

Soil structure has been considered as one of the important factors of soil quality, which influences properties such as soil water retention [35, 36]. From Figure 3.2.7.1, it is clear to see that the soil samples from Hook Village are close to silt while the soil samples from Parys Mountain are more sandy. Both of the sites have only small amounts of clay.

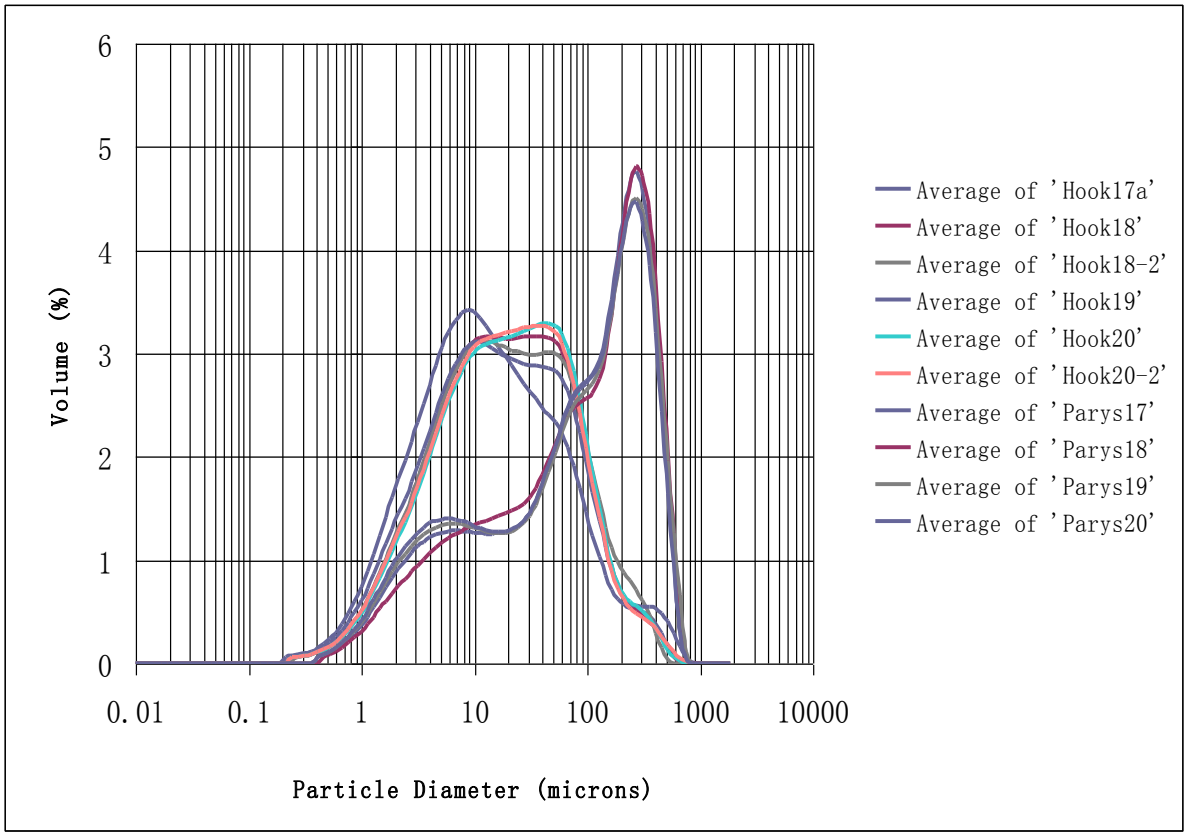


Figure 3.2.7.2 Classification of the soils according to this distribution

Table 3.2.7 particle size distribution of the soil samples

Hook Village		Parys Mountain	
Sample name	Mode particle size (μm)	Sample name	Mode particle size (μm)
Average of Hook17a	9.41	Average of Parys17	286
Average of Hook18	38.6	Average of Parys18	297
Average of Hook18-2	12.8	Average of Parys19	290

Average of Hook19	11.4	Average of Parys20	282
Average of Hook20	46.6		
Average of Hook20-2	39.2		

From the table 3.2.7 above, the mode particle size means the value particle size with the highest occurrence. It can be seen that Parys Mountain has the larger mode particle size by a large margin while Hook village shows the smaller particle size. The reason may be Parys Mountain samples have more sand-sized aggregates (63-2000 μm) (Figure 3.2.7.1). The finding that these samples contain only small amounts of clay is important for interpreting the results of leaching experiments as metal ions may bind to clay minerals and therefore become more difficult to leach. The small amounts of clay in these samples may suggest that the metals may be more readily leached.

3.3 Statistical analysis

3.3.1 Outliers

In the following chapters which describe the leaching experiments, only four soil samples from each site were used to make replicate analyses to get an average of the leaching results. As soil samples are never homogenous, if a result was deemed to be significantly different from the other three, such result was considered to be outlier.

To discard the outliers, tests such as Dixon's test, $4\bar{d}$ test and Grubbs' test are usually used [37]. In this research, as the results are always from four repeats and four is a small sample size, Dixon's test has been selected [38].

Dixon's test (also called the Q-test) is a popular test to calculate outliers. For the sample (size 3 to 7) the test assesses a suspect measurement by comparing the difference between it and the measurement nearest to it in size with the range of the measurements [38]. In order to use Dixon's text for an outlier, all measurements must come from the same population and the statistic Q is calculated:

Q=|suspect value - nearest value| / (largest value – smallest value)

If the calculated value Q exceeds the critical value, that value will be rejected. The critical values of Q for P=0.05 are listed in the following table:

Table 3.3.1 Critical values of Q (P=0.05) for a two sided test [38]

Sample size	*Critical value*
4	*0.831*
5	*0.717*
6	*0.621*
7	*0.570*

Taken from King, E.P.1958.J.Am.Statist.Assoc., 48:531

Here is an example taken from the results detailed in Chapter 4.4 using different concentrations of H_2SO_4 to extract iron from the soil samples. The example shows the

method to decide whether a particular result is an outlier or not.

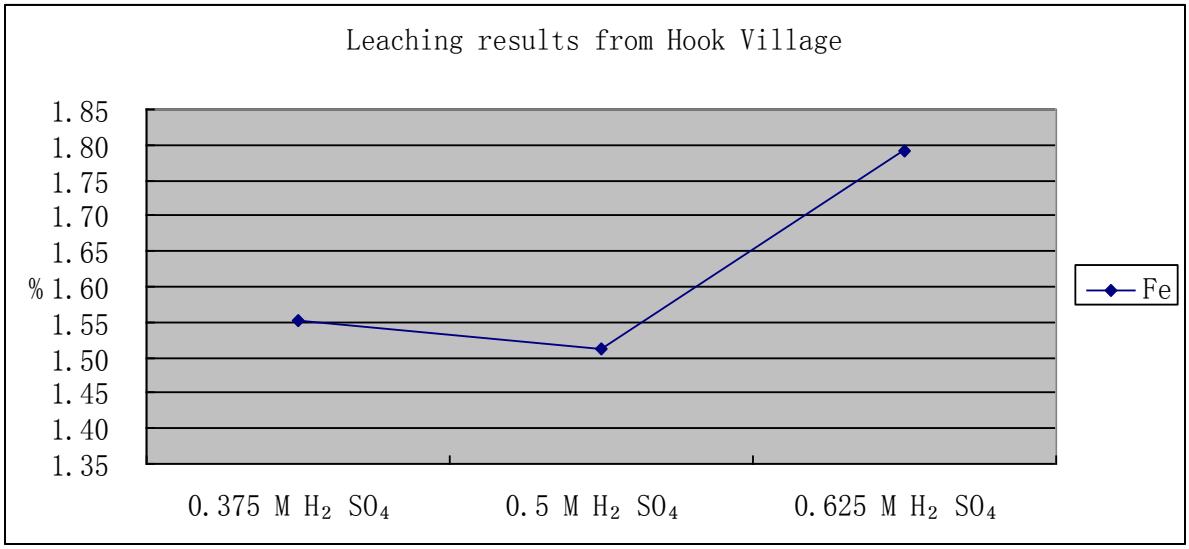


Figure 4.4.4 Trendline of Fe Leached from Hook Village using three additional concentrations (0.375 M H_2SO_4, 0.5 M H_2SO_4, 0.625 M H_2SO_4) of sulfuric acid and detected by AAS

From the results of Chapter 4.3 and 4.4 it is shown that the amount of iron leached from the soil keeps increasing when the concentration of acid is increased. But from Figure 4.4.4 above, it is shown that the amount of iron leached does not increase as the acidity increases. When using 0.5 M H_2SO_4 as matrix, there is a decrease in the curve. As the points used in the figure are the average of each of four repeat results, a method is shown here to check whether the four original values used to calculate the % leaching at a concentration of 0.5 M H_2SO_4 contain an outlier and whether the unexpected point comes from the presence of an outlier.

The point at 0.5 M H_2SO_4 (1.51 %) is an average of four repeat values 1.32 %, 1.57 %, 1.59 % and 1.58 %. Dixon's test can be used to decide whether there is an outlier.

Q value = |suspect value - nearest value| / (largest value – smallest value)

= | 1.32 – 1.57| / (1.59 – 1.32) = 0.926

Checking table 3.3.1 above, it shows that the Q value is larger than the critical value of 4 samples (0.831). So the value 1.32 % is an outlier and could be rejected. When using the other three values to calculate the % leaching at the point 0.5 M H_2SO_4 the average value is 1.58% and the updated figure is shown below:

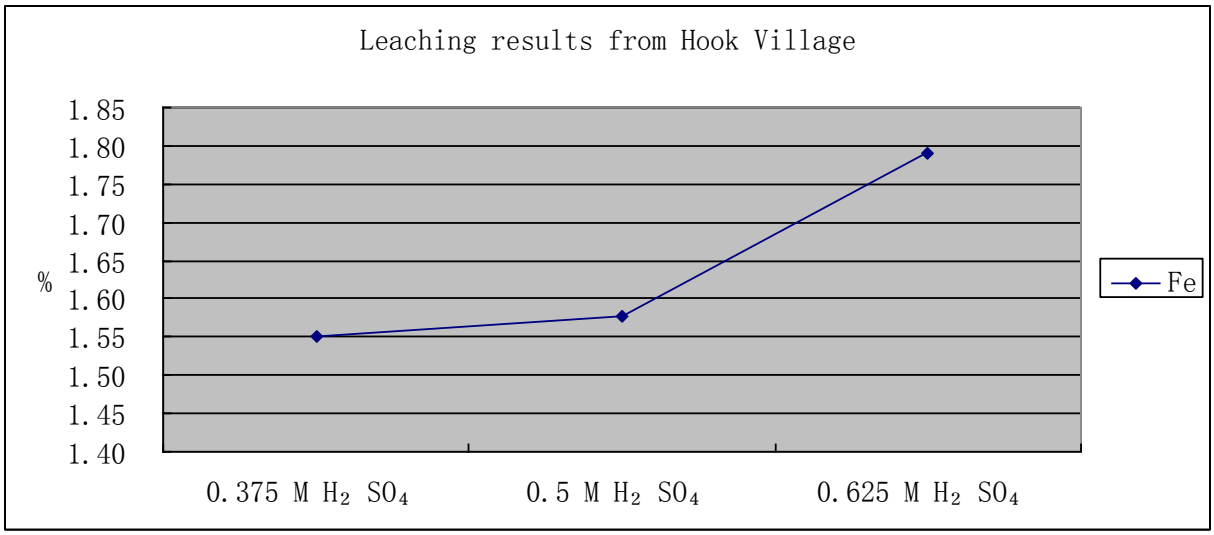


Figure 4.4.5 Trendline of Fe Leached from Hook Village using three additional concentrations (0.375 M H_2SO_4, 0.5 M H_2SO_4, 0.625 M H_2SO_4) of sulfuric acid and detected by AAS

In the following chapters, all results suspected as being outliers will be checked by Dixon's test to decide whether they are outliers or not.

3.3.2 Means and standard deviations calculated for a twenty - repeat experiment

In chapters 3, 4, 5 and 6, four soil samples from each site were used to make replicate analyses to get an average of the leaching results. As soil samples are never homogenous, this “repeat” experiment was designed to show the repeatability of the leaching experiment and to indicate how homogeneous the soil samples are. In order to estimate the likely standard deviation on these values one experiment was carried out in which twenty soil samples from Hook Village were taken as replicates and were leached by 20 mL 0.5 M HCl solution to get a comparison.

Table 3.3.2 the concentrations of Cu, Pb and Zn of twenty soil samples from Hook Village leached by 0.5 M HCl and detected by AAS

Sample number	Concentration of Copper (ppm)	Concentration of Lead (ppm)	Concentration of Zinc (ppm)
533	78.29	261.31	54.63
534	73.01	217.27	49.38
535	78.27	239.26	49.15
536	67.69	212.77	42.68
537	62.09	202.65	42.05
538	62.74	206.01	41.59

539	57.41	187.59	40.44
540	57.63	194.80	39.00
541	56.50	178.38	39.78
542	85.85	192.98	38.69
543	74.24	240.35	50.92
544	60.22	197.04	42.51
545	58.98	193.32	43.17
546	60.06	202.64	39.90
547	65.17	229.28	46.44
548	63.67	217.61	42.38
549	63.26	216.31	43.97
550	60.03	207.30	41.86
551	69.60	241.59	46.77
552	64.38	223.31	41.13
Average	**65.95**	**213.09**	**43.82**

From Table 3.3.2 above, it is easy to see that the twenty samples have similar results but some determinations are a bit higher or lower than others. The mean concentrations and

standard deviations of Cu, Pb and Zn are (65.95 ± 8.14) ppm, (213.09 ± 21.18) ppm, (43.82 ± 4.35) ppm, respectively. The following three figures (Figure 3.3.2.1, Figure 3.3.2.2, Figure 3.3.2.3,) show the distribution of concentrations of each element (Cu, Pb and Zn) from twenty repeats.

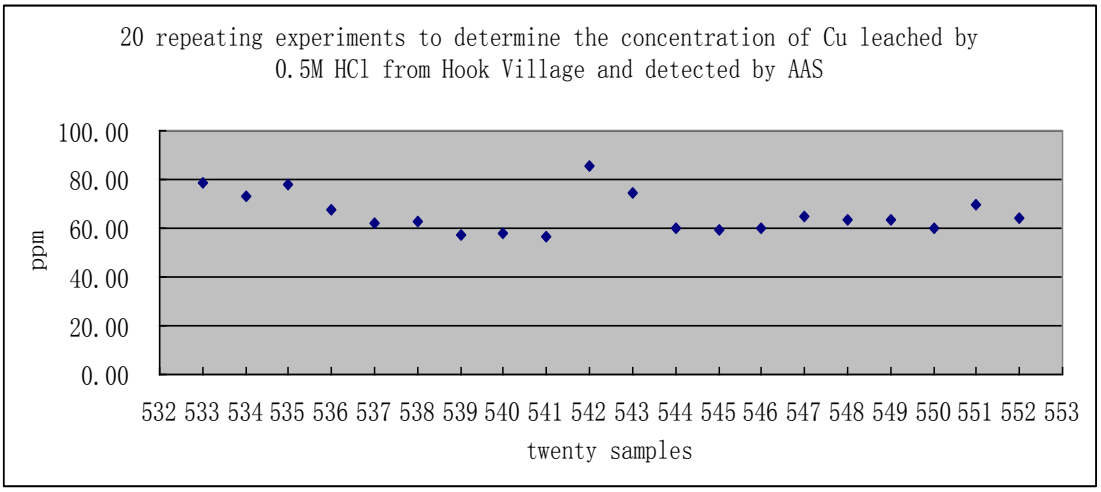


Figure 3.3.2.1 20 repeat experiments to determine the concentration of Cu leached by 0.5 M HCl from Hook Village and detected by AAS

From figure 3.3.2.1, the values of sample 533, sample 535 and sample 542 are significantly bigger than the average ((65.95 ± 8.14) ppm) and the values of samples 539-541 are a bit lower the average. The average copper concentration is (64.54 ± 4.83) ppm if the six samples (533, 535, 539-542) are deleted. If only sample 533, sample 535, sample 541 and sample 542 are deleted, the average of copper concentration is (63.76 ± 5.11) ppm. The three average results are close to each other and it means the twenty samples have good repeatability. The results suggest that inhomogeneity of samples should not have too much effect, in general, on the results reported in this thesis but certain individual results may be affected. The results reported here also show that even if one or two individual results are

out of the range it does not affect the overall average concentrations too significantly.

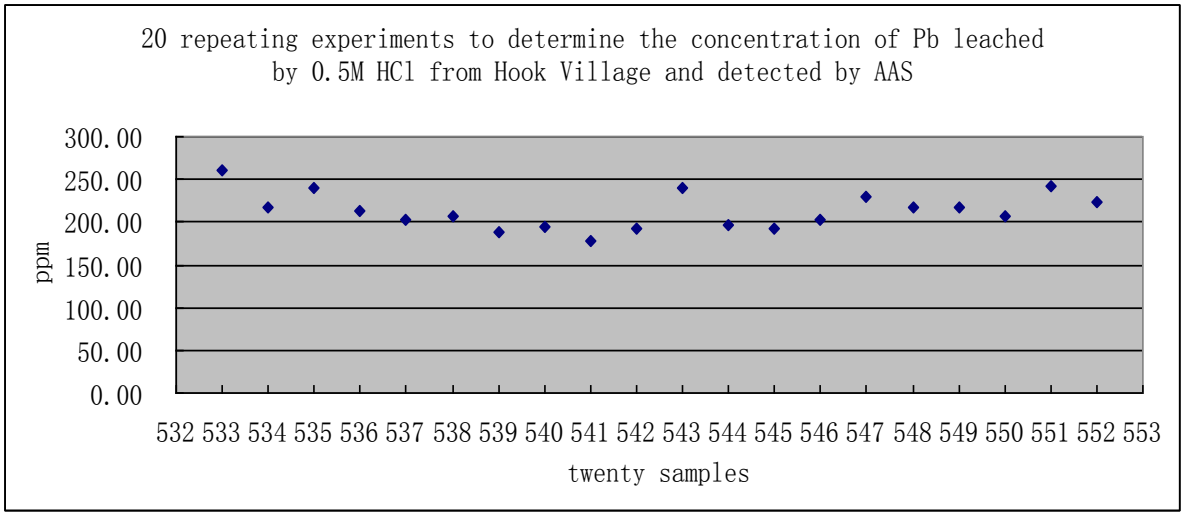


Figure 3.3.2.2 20 repeat experiments to determine the concentration of Pb leached by 0.5 M HCl from Hook Village and detected by AAS

From figure 3.3.2.2, the values of sample 533, sample 535, sample 543 and sample 551 are much bigger than the average ((213.09 ± 21.18) ppm) and the values of sample 539 and sample 541 are a bit lower than the average. The average lead concentration is (208.09 ± 11.62) ppm if these six samples are deleted. If only sample 533, sample 539 and sample 541 are deleted, the average of copper concentration is (213.79 ± 16.46) ppm. The three average results are still close to each other and the conclusions are therefore the same as those for the copper concentrations.

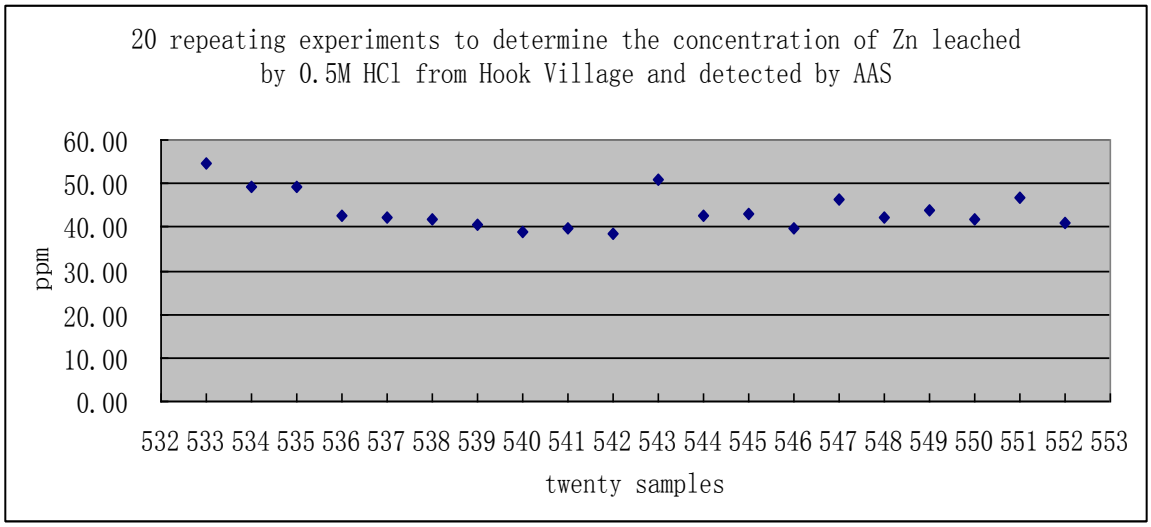


Figure 3.3.2.3 20 repeat experiments to determine the concentration of Zn leached by 0.5 M HCl from Hook Village and detected by AAS

From figure 3.3.2.3, the values of sample 533, sample 534, sample 535 and sample 543 are significantly bigger than the average ((43.82 ± 4.35) ppm) and the values of samples 540 and sample 542 are a bit lower than the average. The average zinc concentration is (42.48 ± 2.12) ppm if the six sample are deleted. If only sample 533 sample, 542 and sample 543 are deleted, the average zinc concentration is (43.07 ± 3.13) ppm. The three average results are still close to each other.

It was not possible (because of time and equipment constraints) to carry out 20 repeats of *every* measurement made in this thesis. As mentioned previously, four repeats were made of each measurement. In the next section a comparison is made of the average concentration and the standard deviation for the 20-repeat measurements and for sub-sets of four repeats selected from these 20 repeats. The following table shows the averages and standard deviations that are obtained when sub-sets of four of the twenty samples are selected:

Table 3.3.3 the averages and standard deviations of Cu, Pb and Zn of twenty soil samples from Hook Village leached by 0.5 M HCl

Sample number	Average of Cu (ppm)	standard deviations of Cu (ppm)	Average of Pb (ppm)	standard deviations of Pb (ppm)	Average of Zn (ppm)	standard deviations of Zn (ppm)
533-552	65.95	8.14	213.09	21.18	43.82	4.35
533-536	74.32	5.07	232.65	22.34	48.96	4.89
537-540	59.97	2.84	197.76	8.25	40.77	1.36
541-544	69.20	13.47	202.19	26.67	42.97	5.54
545-548	61.97	2.93	210.71	15.91	42.97	2.70
549-552	64.32	3.98	222.13	14.53	43.43	2.53

As mentioned previously it was impossible to have twenty repeats for every experiment, and in the following leaching experiments which are reported in chapters 3, 4, 5 and 6 there were only four repeats. From the Table 3.3.3 above, it is shown that on the whole when only 4 samples were used as repeats, the average shows some differences and the standard deviation shows some variation often actually being improved. It must be remembered that a process to discard outliers has already been developed.

The overall conclusion is that it would be, of course, desirable to have 20 repeats of every measurement but that practically and pragmatically it is possible to obtain meaningful data with only four repeats for each measurement.

3.3.3 Confidence limits of the mean for samples

In chapter 3.3.2, for all of the repeat results, a mean value and standard deviation were calculated. The confidence interval also plays an important role in statistical analysis within which it can reasonably be assumed the true value is included. The extreme values of the confidence interval are called confidence limits. In analytical chemistry, the confidence interval is always taken as 95 % or 90 % [37] and here a 95% confidence interval was chosen.

The confidence limits of the mean for small sample sizes are given by [38]:

$$\bar{x} \pm t_{n-1}\, s / \sqrt{n}$$

Here is shown an example of calculating the confidence limits. From the results of Table 3.3.2, for twenty repeat experiments of Cu concentrations, the mean value is $\bar{x}$=65.95 and the standard deviation is S=8.14. If confidence interval is 95 %, the confidence limit is following:

$$\bar{x} \pm t_{n-1}\, s / \sqrt{n} = 65.95 \pm t_{20-1} * 8.14 / \sqrt{20} = 65.95 \pm 2.095 * 8.14 / \sqrt{20}$$

$$= 65.95 \pm 3.81$$

So the mean concentration of Cu should be shown as 65.95 **±** 3.81 ppm (confidence interval 95 %).

3.4 Physical effects of soil samples

Using the steps detailed above, the composition of the soil samples from Hook Village and Parys Mountain have been determined. These results show that chemical effects can affect the leaching results. In this part of the research, experiments have been done to determine the effect of the physical nature of the soil samples on the leaching results. The soil samples from two different sites have been put in two groups: ground samples and unground samples. Leaching experiments were carried out using a series of different acid matrices with the same leaching process to compare the leaching results. Two different acids and total of eight different solutions (0.05 M HCl, 0.1 M HCl, 0.25 M HCl, 0.5 M HCl, 0.025 M H_2SO_4, 0.1 M H_2SO_4, 0.25 M H_2SO_4 and 0.5 M H_2SO) were selected as matrices. The following table shows the comparison of copper results as an example.

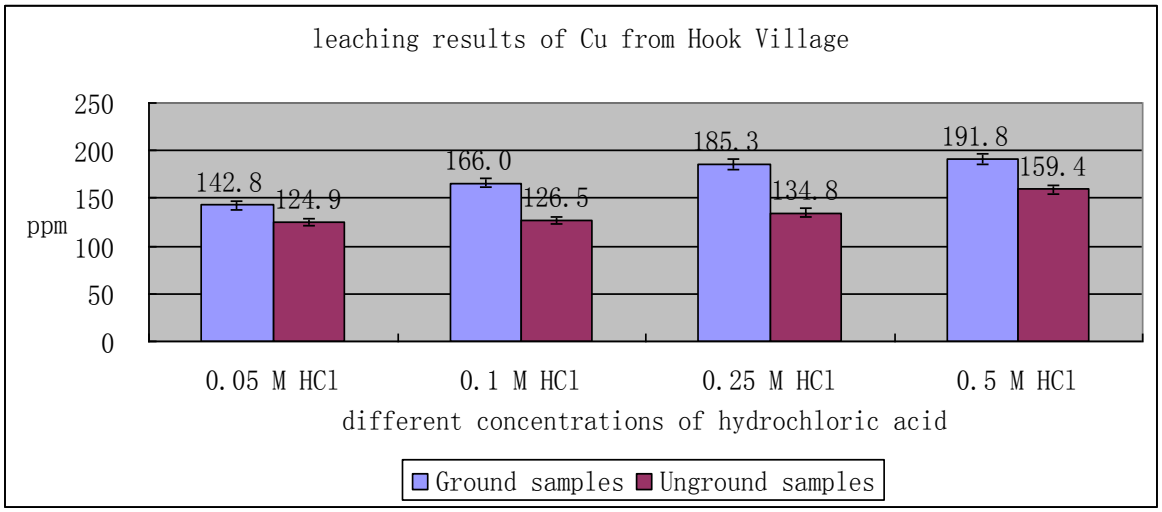


Figure 3.4.1 A graph showing the concentrations of Cu leached from Hook Village using 0.05 M HCl, 0.1 M HCl, 0.25 M HCl and 0.5 M HCl and detected by AAS

From Figure 3.4.1, when using different concentrations of hydrochloric acid as matrices, for both the ground and unground samples from Hook Village, the increase of HCl solution concentration leads to more copper ions being leached out. It also shows that the physical state can affect the leaching results. In all cases the ground samples show higher concentrations of copper in the leachate than do the unground samples.

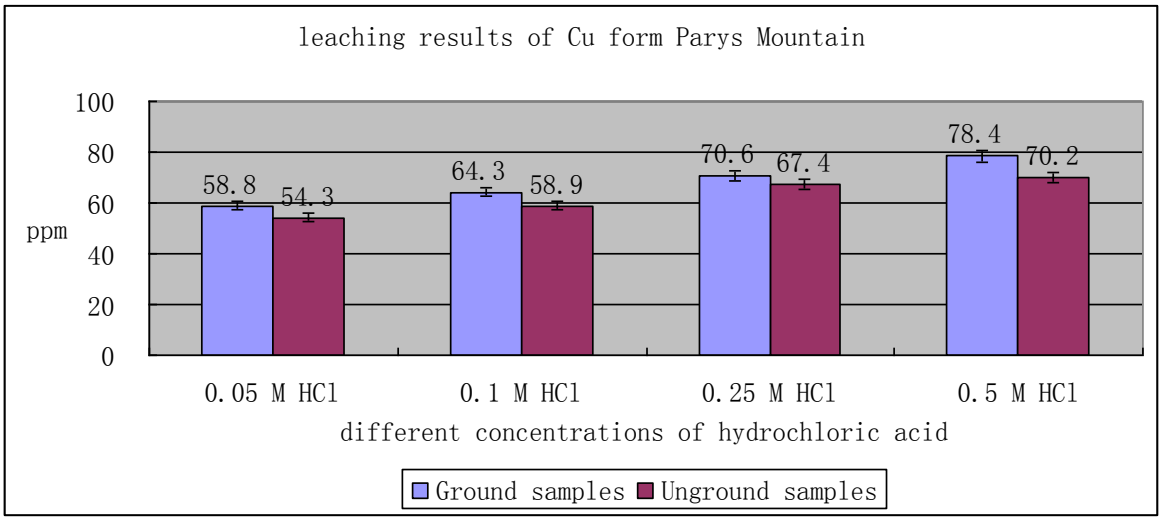


Figure 3.4.2 A graph showing the concentrations of Cu leached from Parys Mountain using 0.05 M HCl, 0.1 M HCl, 0.25 M HCl and 0.5 M HCl and detected by AAS

From Figure 3.4.2, when the soil samples from Parys Mountain are investigated, the same conclusion can be found: the physical state can affect the leaching results. When using hydrochloric acid as matrices, comparing the leaching results with the same concentration, more copper from ground samples has been leached out.

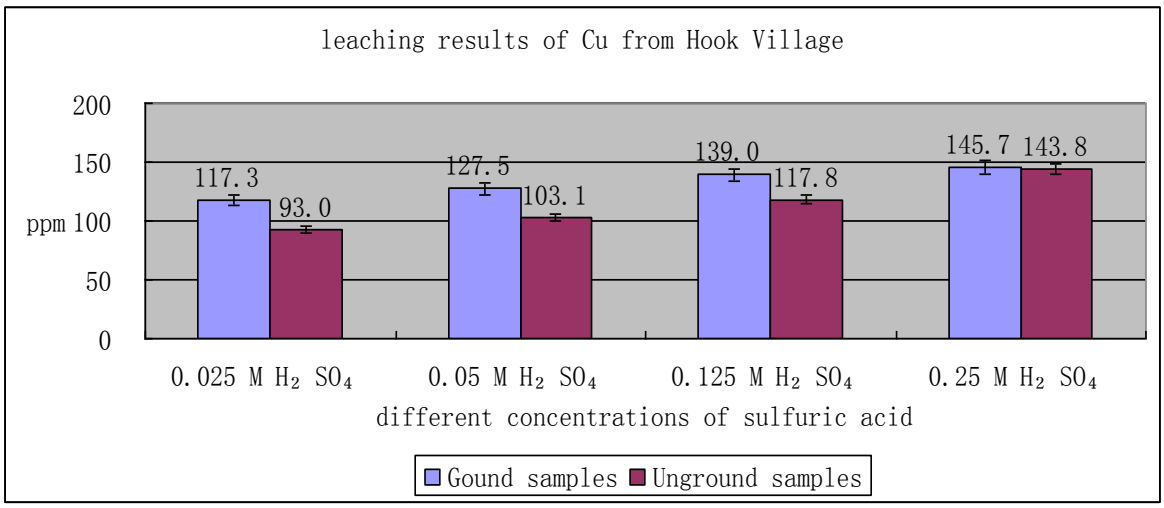


Figure 3.4.3 A graph showing the concentrations of Cu leached from Hook Village using 0.025 M H_2SO_4, 0.1 M H_2SO_4, 0.25 M H_2SO_4 and 0.5 M H_2SO_4 and detected by AAS

From Figure 3.4.3, when using different concentrations of sulfuric acid as matrices for ground and unground samples from Hook Village, the increase of H_2SO_4 concentration to more copper ions being leached out and the ground samples show higher concentrations of copper in the leachates.

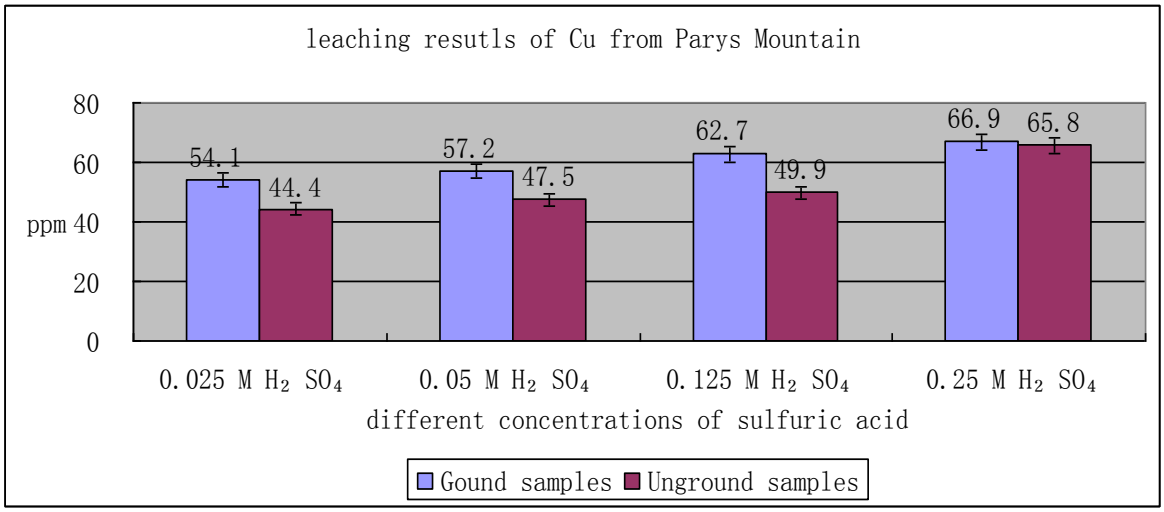


Figure 3.4.4 A graph showing the concentrations of Cu leached from Parys Mountain using 0.025 M H_2SO_4, 0.1 M H_2SO_4, 0.25 M H_2SO_4 and 0.5 M H_2SO_4 and detected by AAS

From Figure 3.4.4, when the soil samples from Parys Mountain are considered, the same conclusion can be found: more copper is leached from ground samples. This confirms that the physical state can affect the leaching results.

3.5 Discussion and conclusion

In this chapter, a preliminary series of analytical experiments has been carried out to determine the composition of the soil samples from two environmentally-important sites Hook Village and Parys Mountain.

Firstly, the soil samples were characterized by measurement of water content, organic content, carbonate content and, pH value. Hook Village samples have higher water content and organic content (water content: 3.41 % ± 0.025 %, organic content: 9.07 % ± 0.17 %) than Parys Mountain samples (water content: 1.41 % ± 0.039 %, organic content: 4.41 % ± 0.38 %). For the carbonate content, from the results of XRF and thermal analysis, the samples will be a mixture of calcium and magnesium carbonates so the actual carbonate content will be somewhere between the values calculated for pure $CaCO_3$ and pure $MgCO_3$. If it is assumed that all of the carbonate content is from calcium carbonate, Hook Village samples have 3.10 % ± 0. 43 % calcium carbonate content while Parys Mountain samples have 1.45 % ± 0.38 % calcium carbonate content. If it is assumed that all of the carbonate content is from magnesium carbonate, Hook Village samples have 2.60 % ± 0. 36 % magnesium carbonate content while Parys Mountain samples have 1.21 % ± 0.32 % magnesium carbonate content. To determine the pH value of the soil samples, two group experiments have been done by mixing different amounts of soil samples (0.5 g and 2 g) with 20 ml of deionised water. The results show that the pH value

changed as different amounts of soil were used. But from both results, there is an observation that the Hook Village samples are more acidic (0.5 g: 6.12 ± 0.06, 2 g: 5.18 ± 0.10) and the Parys Mountain samples are bit alkaline (0.5 g: 7.40 ± 0.06, 2 g: 7.24 ± 0.11).

Secondly, Infrared Spectroscopy (IR) has been used to identify some of the minerals present in the soil samples. From the Figures 3.2.3.1 to Figure 3.2.3.3, it is easy to find that quartz and clay minerals are present in both samples, as indicated by the sharp doublet at 778 cm^{-1} and 797 cm^{-1} and υ(Si-O) at 1000-1100 cm^{-1}. Parys Mountain may contain a sulphate-containing mineral, probably barite ($BaSO_4$) or gypsum ($CaSO_4$) as there are some peaks between 1040-1210 cm^{-1} which probably come from the υ(SO_4^{2-}) asymmetric stretching vibration. There is also evidence of $CaCO_3$ or $MgCO_3$ in the samples studied here which is characterized by bands around 1409 cm^{-1} from the asymmetric stretching of the carbonate ion. This results back up to the thermal analysis.

Thirdly, XRF has been done to determine which specific metals contaminate the soils and the concentrations of these metals in each sample. This work also allowed elements to be selected for leaching experiments. Oxygen, silicon and aluminium are the highest content elements in the earth crust. Silicon and aluminium are found from both sites samples in a high level (Hook Village: Al: 7.56±0.06 %, Si: 32.25±0.17 %, Parys Mountain: Al: 2.42± 0.12 %, Si: 39.15±1.04 %). Iron is the second most abundant metal in the Earth's crust and it is also a good element on which to perform leaching experiments as it is readily extractable as Fe^{2+} ion under acid conditions. Both sites' samples contain varying degrees of potassium, sodium, manganese and titanium and the soils also have varying trace quantities of chromium, cobalt and nickel. As Parys Mountain is known to be a major copper-mining area, its concentration of copper (95.8 ppm) is nearly four times higher than mean value for the whole of Wales (23.23 ppm). But an interesting finding is that the Hook Village samples show higher levels of copper (225.0 ppm) than the Parys Mountain samples. Hook Village was a coal mining area in the 19th century. This may simply mean

that coal mining activity can lead to more pollution and the mining working in Parys Mountain has been efficient at extracting the copper before adding the waste to the spoil tips. The amounts of calcium and magnesium in both sites are not too high but these results can be compared with the results of thermal analysis and IR spectroscopy. It is confirmed that these soil samples contain a mixture of calcium and magnesium carbonates. Partly on the basis of elemental analysis by X-ray Fluorescence, copper, zinc, iron and lead were selected as representative metals to study in leaching experiments.

Leaching experiments have played a central role in this research. The following chapters report experiments using various matrices to find out the chemical effects on leaching. In this chapter, atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) were used to analyse leachate solutions. The results show the concentration of given metals (Cu, Zn, Pb and Fe) and can be compared with the results from XRF. In this chapter, four different solutions (0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, 0.1 M EDTA-2Na,) were selected as matrices. The given metals can be leached out by the four matrices. EDTA is a poorer leachate than the other three acids. But for Pb, sulfuric acid was the poorest leachate. When determined by AAS, sulfuric acid only leached 50 % of the amount of lead that hydrochloric acid leached (HCl: 292 ppm, H_2SO_4: 147ppm) from Hook Village and 59 % (HCl: 220 ppm, H_2SO_4: 129ppm) from Parys Mountain. The reason is probably that lead sulfate ($PbSO_4$) is only very slightly soluble in water (42.5 mg / L at 25 °C) while lead chloride ($PbCl_2$) is much more soluble (9.9 g / L at 25 °C). This result suggests that the solubility of $PbSO_4$ is limiting the amount of Pb that can be leached in H_2SO_4. In dilute acid, the solubility of $PbSO_4$ has a small increase. The relevant equations are:

$$H_2SO_4\,(aq) \rightleftharpoons HSO_4^-\,(aq) + H^+\,(aq),$$

$$HSO_4^-\,(aq) \rightleftharpoons SO4^{2-}\,(aq) + H^+\,(aq),$$

$$Pb^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow PbSO_4\,(s)$$

The leaching results of Cu, Zn and Pb from ICP-MS are generally similar to the results from AAS. However, there are some differences between the results from AAS and ICP-MS. Such as in Figure 3.2.6.7, when using 0.375 M H_2SO_4 as matrices, the value for Cu determined by AAS is a bit lower than the value determined by ICP. One reason may be when the leachates diluted 100 times to determine by ICP, the big dilution factor may add some errors.

It is shown that chemical parameters can affect the leaching results, and some comparison experiments have also been done to detect the effect of the physical nature of the soils on the leaching results. Ground and unground samples were used as a control test with the same leaching process to compare the leaching results. It is found that higher concentrations of metals are leached from the ground samples. To back up this finding particle size analysis was done to determine the size distribution for each sample.

In this research, four soil samples from each site were used as replicates to get an average for every measurement in the leaching results. As soil samples are never homogenous, a twenty-repeat experiment was also done to estimate the repeatability of the leaching experiment. It was decided on the basis of these results that in the following leaching experiments described in chapters 3, 4 and 5 where only four repeats were carried out, if one result is much higher or lower than the other three, it is reliable to delete this result and to calculate an average only using the other three.

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Chapter 4 Leaching Experiments Carried out Using Inorganic Acids

4.1 Introduction

Leaching experiments have played the main role in this project. Leaching tests are fundamental tools for the assessment of contaminated soil. Generally, acidification is a useful process for the recovery of heavy metals from contaminated soil [1]. Acidification can be carried out by mixing wastes with acids such as hydrochloric acid and sulfuric acid, the process is named as chemical leaching [1]. In this way different concentrations of each metal may be leached from the soil when using different matrices. The extraction efficiency can be increased by adding acids [2]. The reason for this may be that acids can dissolve carbonates in soil and metal-bearing fractions, they can exchange heavy metals from soil surfaces [3]. They can also dissolve oxides, sulfides, hydroxides and so on.

When carrying out leaching experiments, the pH value and stirring time should be controlled as they are all very important parameters. In 2010, Bayat et al evaluated microbial and chemical leaching processes for heavy metal removal from dewatered metal plating sludge [4]. The purpose of that study as described in this paper was to evaluate the application of the bioleaching technique involving Acidithiobacillus ferrooxidans to recover heavy metals (Zn, Cu, Ni, Pb, Cd and Cr) in dewatered metal plating sludge (with no sulfide or sulfate compounds). In these experiments, the results demonstrated that both conditional (such as pH for chemical, sulfate production for bioleaching) and operational (pulp density and agitation time for leaching) parameters were all important parameters in leaching processes. So in the project described in this thesis, the agitation time was fixed as a certain time such as 24 hours and the pH value was controlled to get a better comparison of mobilities of different metals as a function of pH.

There is another experiment which has shown that the pH value is one of the key parameters that determines heavy metal mobility in soils. It is also noted that different types of tests are available to assess pH-dependent leaching such as the toxicity characteristic leaching procedure (TCLP) [5, 6]. In 2008, Cappuyns et al showed the use of pHstat leaching tests as a tool to assess the potential mobilisation of trace metals from soils. The European pHstat test, which is currently being standardized within the CEN framework (CEN-TC292/WG6,) consists of a 48 h pHstat test at 8 different pH-values in the range 4–12 [7]. The kinetic rate of release of metals during pHstat indicated that the metals' release was also related to the oxidation state. A pHstat test allows one to assess how the solubility changes if in situ pH changes occur. Moreover, information is obtained on the potential buffering capacity of the sample and its sensitivity to pH changes as a result of external stresses.

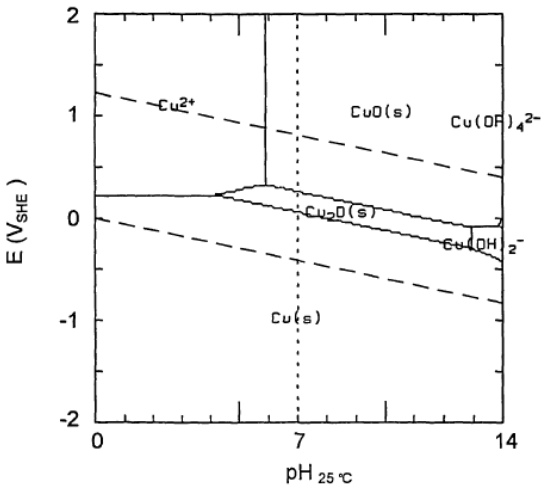


Figure 4.1.1 Pourbaix diagram of Cu at 25 °C from reference [8]

Figure 4.1.1 shows the Pourbaix diagram of Cu. The upper line shows the oxygen equilibrium line and potentials above this line results in oxygen evolution. The lower line shows the hydrogen line and potential below this line results in hydrogen evolution. It can be seen that at pH values below about 6 and in oxidizing environments copper will exist as Cu^{2+} ions which are comparatively mobile. By contrast in alkaline pH it will tend to exist

as immobile oxides and in reducing conditions as immobile copper metal [8, 9].

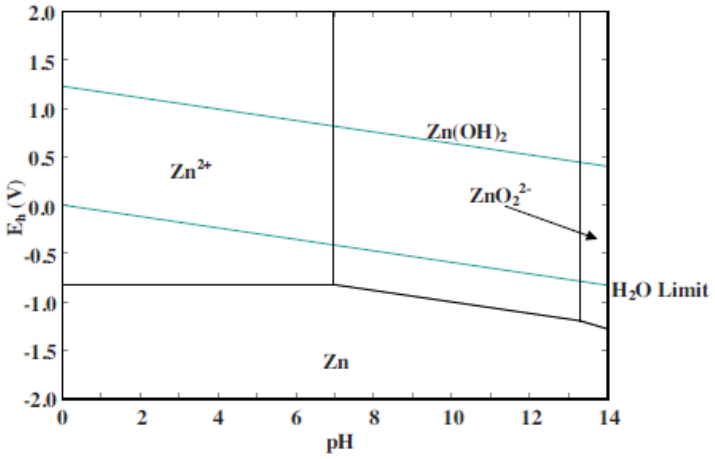


Figure 4.1.2 Pourbaix diagram of Zn at 25 °C from reference [10]

Figure 4.1.2 shows the Pourbaix diagram of Zn. It is clear to see that at pH values below about 7 the zinc will exist as Zn^{2+} ions which are comparatively mobile. By contrast, zinc hydroxide is stable in alkaline pH (range 7-13) and it will tend to be immobile [10, 11].

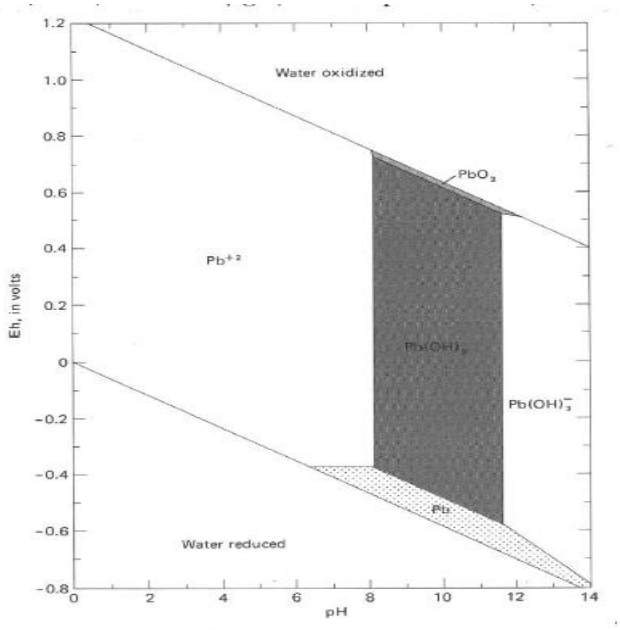


Figure 4.1.3 Pourbaix diagram of Pb -H_2O system at 25 °C from reference [12]

Figure 4.1.3 shows the Pourbaix diagram of Pb. It can be seen that at pH values below about 8 the Pb will exist as Pb^{2+} ions which are comparatively mobile while lead hydroxide is stable at pH values above 12. On the other hand, oxidized solid PbO_2 is stable only in a highly oxidizing environment [12, 13, 14, 15].

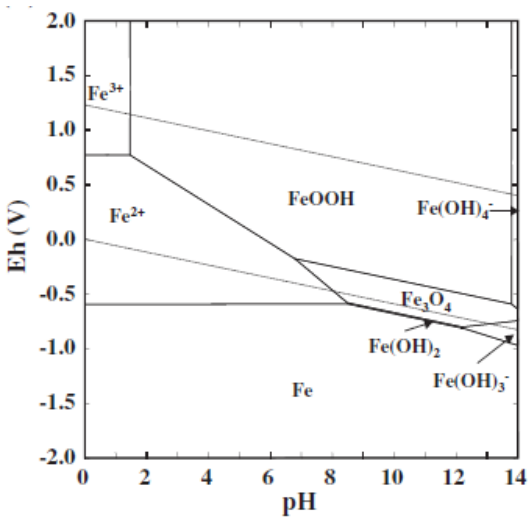


Figure 4.1.4 Pourbaix diagram of Fe -H_2O system at 25 °C from reference [16]

Figure 4.1.4 shows the Pourbaix diagram of Fe. It can be seen that the Fe^{2+} and Fe^{3+} are stable in acidic conditions and are comparatively mobile. Fe^{3+} exists undermore oxidizing conditions. By contrast in alkaline pH iron will form FeOOH, Fe_3O_4 and iron hydroxides which are all relatively immobile [16, 17].

For chemical leaching, choosing suitable matrices is very important. Inorganic acids such as H_2SO_4, HCl or HNO_3 were usually used as matrices in the work described here but some organic acids can also give interesting results. EDTA and HCl are common leaching agents used for heavy metals. In 2012, Udovic's experiments showed that EDTA is more efficient than HCl: up to 133-times lower concentration of the chelant than of HCl was needed for the same percentage (35%) of Pb removal [18]. As expected, HCl significantly

dissolved carbonates from calcareous soil, while EDTA leaching increased the pH of the acidic soil. In remediation with soil leaching, a pool of more mobile heavy metals is extracted in solution for further disposal or treatment. The extraction efficiency can be enhanced by adding acids, chelating agents such as EDTA or surfactants to the leaching solution. Acids dissolve carbonates and other metal-bearing fractions and exchange heavy metals from soil surfaces, thus increasing their extractability. So in this project, EDTA and HCl will be used as matrices. And from Udovic's results, the calcium carbonate content of each soil sample should be determined as this may affect leaching results. The details of leaching experiments involving EDTA can be seen in chapter 5.

There may be some relationship between the mobility of the metals and the composition of the soil. In 2012, Kumar et al conducted research about the potential mobility of heavy metals [19]. In that research, they first examined the mobility characteristics of Cu, Zn, and Pb through soil. The results showed that a gradual increase in pH and a decrease in dissolved organic carbon had a pronounced effect on the mobilization of heavy metals. Pb showed the highest retention compared to Cu and Zn which implies that metal complexes play a pivotal role in metal transport. So in this project, a preliminary series of experiments was done to measure the organic content and calcium carbonate content in the samples as they may affect the results of leaching (see Chapter 3).

Lead is an important heavy metal in soil pollution and has been studied extensively in this project. In 2011, Park et al showed that the mobility of lead in soils can be mitigated by its immobilization using both soluble and insoluble phosphate compounds [20]. The leaching of lead increased when the soils were amended with soluble phosphorus compounds such as potassium dihydrogen phosphate, because soluble phosphorus compounds increase Pb mobility.

Besides lead, zinc was another heavy metal which was always used for leaching experiments. Some experiments show that phosphate could accelerate the vertical migration of heavy metals in soils and also organic carbonate content will affect the results of leaching. In 2009, Zhang et al conducted research to evaluate the effects of long-term

application of phosphorus fertilizers on the mobility of dissolved organic matter and heavy metals in agricultural soils [21]. The soils were spiked with ammonium phosphate at application rates of 0, 25, 50, 100, 250, and 500 mg phosphorus per kilogram of soil and by experiment these workers found that the water extractable organic carbon content in soils increased significantly with increasing rates of phosphorus application. Also, high rates of phosphate applications could cause an increase in the dissolved organic matter concentrations in the leachates. Maybe due to the formation of metal complexes, the concentrations of copper, cadmium, and zinc in the leachates were positively correlated with dissolved organic matter. In contrast, lead concentrations in the leachates were negatively correlated with dissolved organic matter, and decreased with increasing rates of phosphate applications [21]. In this chapter, different concentrations of phosphate are considered.

Atomic Absorption Spectroscopy (AAS, Nov AA 350 Analytik Jena. room temperature) has been used for the analysis of the leachate solutions. A gradual decrease in pH has been shown have an obvious effect on the mobilization of heavy metals [22]. However, there are two questions:

Does the amount of metal leached from an individual soil sample increase as the acidity increases?

If acids with different anions such as Cl^-, SO_4^{2-} and NO_3^- but with the same acidity are used, do they have the same efficacy of soil leaching?

In this project, hydrochloric acid, sulfuric acid and nitric acid have been used as matrices for leaching experiments. For each inorganic acid, various concentrations have been selected to compare the leaching results. Also, as aqua regia is a stronger acid, it has been selected to compare the leaching results with the overall concentrations of metals within the samples detected by XRF.

4.2 Aqua regia

Aqua regia is a mixed acid made by mixing concentrated hydrochloric acid and nitric acid with a volume ratio 3:1. In this chapter, aqua regia has been made by using concentrated HCl (MW: 36.36, Code: H/ 1150/ PB17, Lot: 1529618, d = 1.18, 37 %) and concentrated HNO_3 (MW 63.01, Code: N/ 2300/ PB17, Lot: 1498983, d = 1.42, 70 %). For each sample, 15 mL HCl solution and 5 mL HNO_3 solution have been mixed.

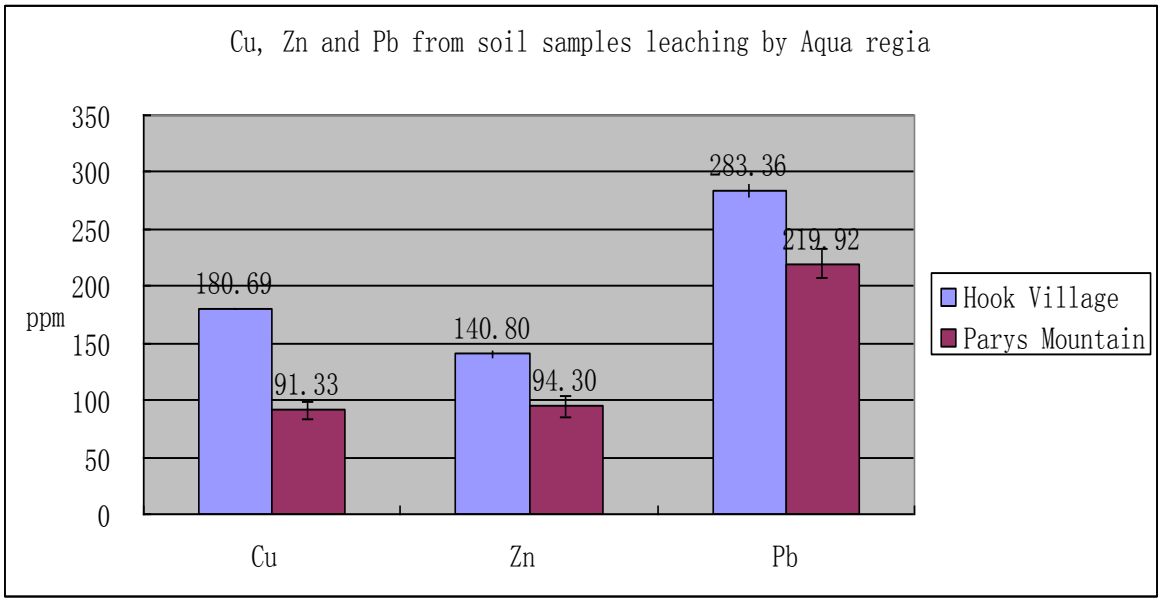


Figure 4.2.1 Value Cu, Zn and Pb leached from Hook Village and Parys Mountain soil samples by using Aqua regia

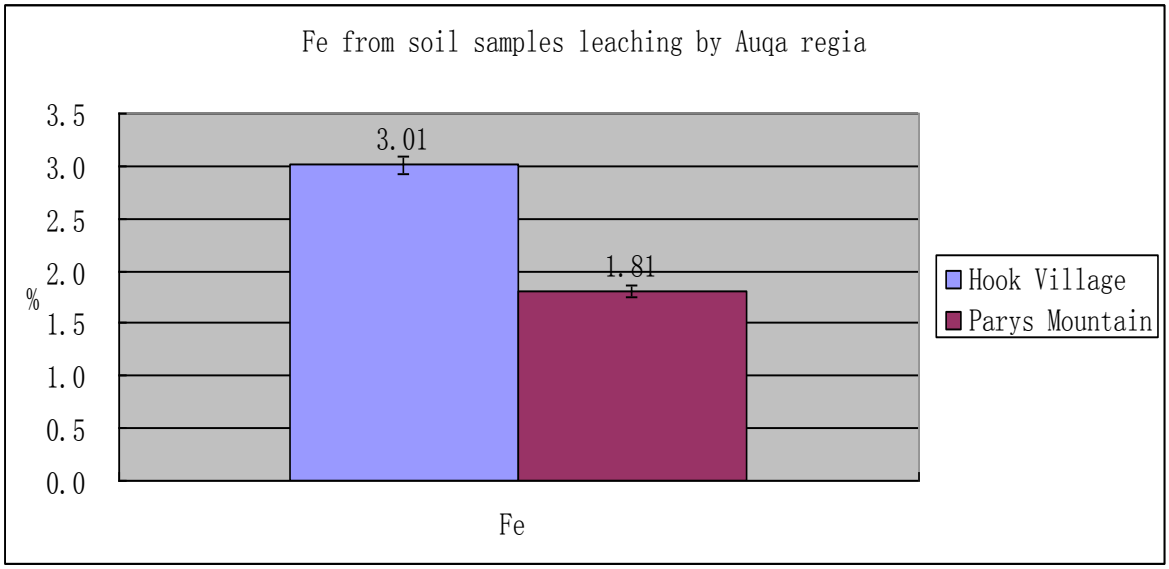


Figure 4.2.2 Percentage of Fe leached from Hook Village and Parys Mountain soil samples by using Aqua regia and detected by AAS

Table 4.2 Average concentration of four metals (Fe, Cu, Zn and Pb) in soil samples from Hook village and in Parys Mountain leaching by Aqua regia detected by AAS and compared with the results determined by XRF

	Fe	Cu	Zn	Pb
Hook village extracted by AR	3.01%	180.69 ppm	140.80 ppm	283.36 ppm
Hook village determined by XRF	4.69%	225.0 ppm	309.0 ppm	378.5 ppm
Percentage of metal extracted by AR compared with by XRF	**64.18%**	**80.31%**	**45.57%**	**74.86%**

Payrs Mountain by AR	1.81%	91.33 ppm	94.30 ppm	219.92 ppm
Payrs Mountain by XRF	2.56%	95.8 ppm	103.0 ppm	263.5 ppm
Percentage of metal extracted by AR compared with by XRF	**70.70%**	**95.33%**	**91.55%**	**83.46%**

Compared with the XRF results from chapter 3 section 3.2.4 (Table 3.2.4.3), it is easy to see that aqua regia is a very strong acid and a very efficient leachate. But it still can not leach out all the heavy metals from the soil samples. For Hook Village, about 64.17% of Fe, 80.31 % of Cu, 45.57 % of Zn and 74.86 % of Pb has been extracted out. For Parys Mountain, 70.70 % of Fe, 95.33 % of Cu, 91.55 % of Zn and 83.46 % of Pb have been extracted out.

For both sites, aqua regia can extract out a large amount of Cu and Pb from the soil samples. But for Zn, there are some differences. The soil samples from Hook Village show only 45.57 % leaching of Zn, but the samples from Parys Mountain show 91.55 % leaching. The reason is perhaps that Zn in the two sites exists as different zinc compounds. In nature zinc is widely distributed. The abundance in the Earth's crust is about 70 ppm. So the samples from Hook village were strongly contaminated by zinc (309 ppm). The principal ores in nature are sphalerite or zinc blende (ZnS), gahnite ($ZnAl_2O_4$), calamine ($Zn_4(H_2O)[Si_2O_7](OH)_2$), smithsonite ($ZnCO_3$), franklinite ($ZnFe_2O_4$) and zincite (ZnO) [23]. The hypothesis is that if the zinc in Parys Mountain is present in an area as a carbonate such as smithsonite it will be easy to leach out by aqua regia whereas the other minerals will be more difficult to leach. Sadly it was not possible to confirm this hypothesis by identifying specific minerals in the samples. Experiments utilizing powder X- ray diffraction were carried out but the diffraction patterns were dominated by peaks from quartz which is highly crystalline and abundant and it was impossible to identify minor

mineral components.

4.3 Different concentrations of hydrochloric acid (HCl)

In this part, dilute HCl solutions were used as matrices and increasing concentrations of HCl have been used to find which concentration was most efficient at leaching metals from soil.

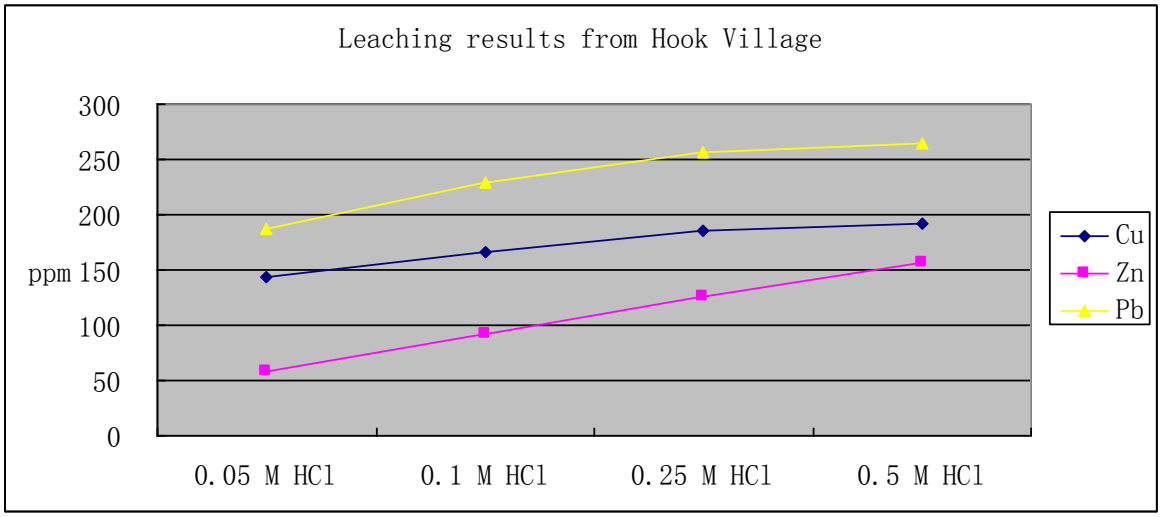


Figure 4.3.1 Trendlines of Cu, Zn, Pb Leached from Hook Village soil samples by using four different concentrations (0.05 M, 0.1 M, 0.25 M, 0.5 M) of hydrochloric acid and detected by AAS

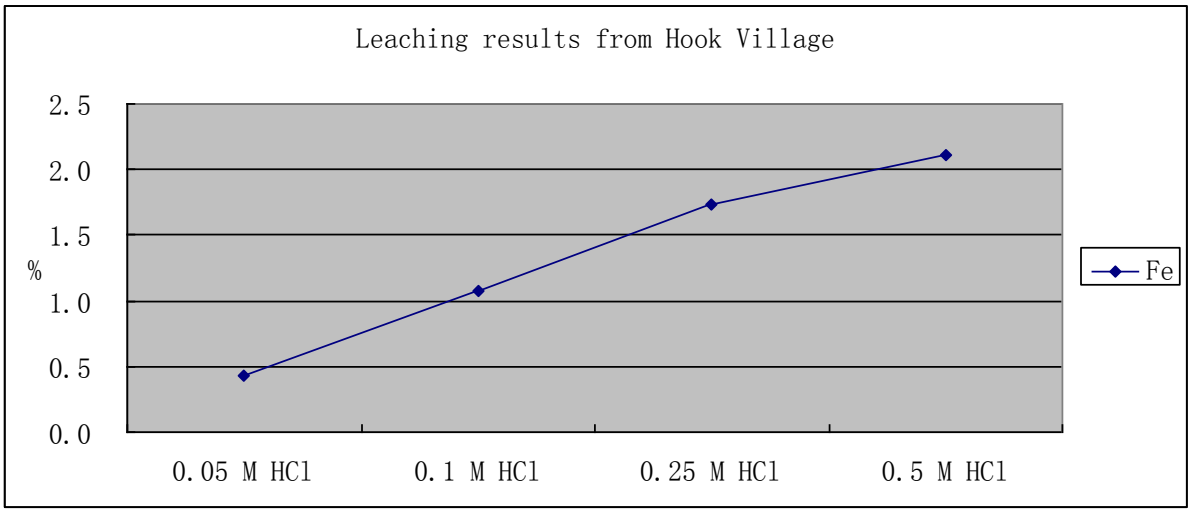


Figure 4.3.2 Trendline of Fe leached from Hook Village using four different concentrations (0.05 M, 0.1 M, 0.25 M, 0.5 M) of hydrochloric acid and detected by AAS

Table 4.3.1 Concentrations of Cu, Zn, Pb Leached from Hook Village soil samples by using four different concentrations (0.05 M, 0.1 M, 0.25 M, 0.5 M) of hydrochloric acid

HCl	Cu (ppm)	Zn (ppm)	Pb (ppm)	Fe %
0.05 M	143	58	187	0.43
0.1 M	166	92	229	1.08
0.25 M	185	125	256	1.74
0.5 M	192	156	264	2.11

From the Figures 4.3.1 and 4.3.2 it is easy to see that when using HCl solution that the increase of HCl solution concentration leads to more metal ions being leached out. And comparing this result with XRF results, nearly 85% of the copper ion has been extracted

out, nearly 50 % of the zinc ions, 69 % of the lead ions and 45 % of the iron ions have been extracted out. Also it shows for copper and lead, when using 0.25 M HCl and 0.5 M HCl as matrices, the amount of metal leached does not increase significantly. The leaching results for copper in 0.25 M HCl solution is 185 ppm while in 0.5 M HCl solution it is 192 ppm. And the leaching results for lead in 0.25 M HCl solution is 256 ppm while in 0.5 M HCl solution it is 264 ppm. So a further three different concentrations of HCl were used to find whether 0.5 M HCl solution is already the maximum concentration for the leaching experiment and above which concentration there is no further increase in concentration of the leached metals.

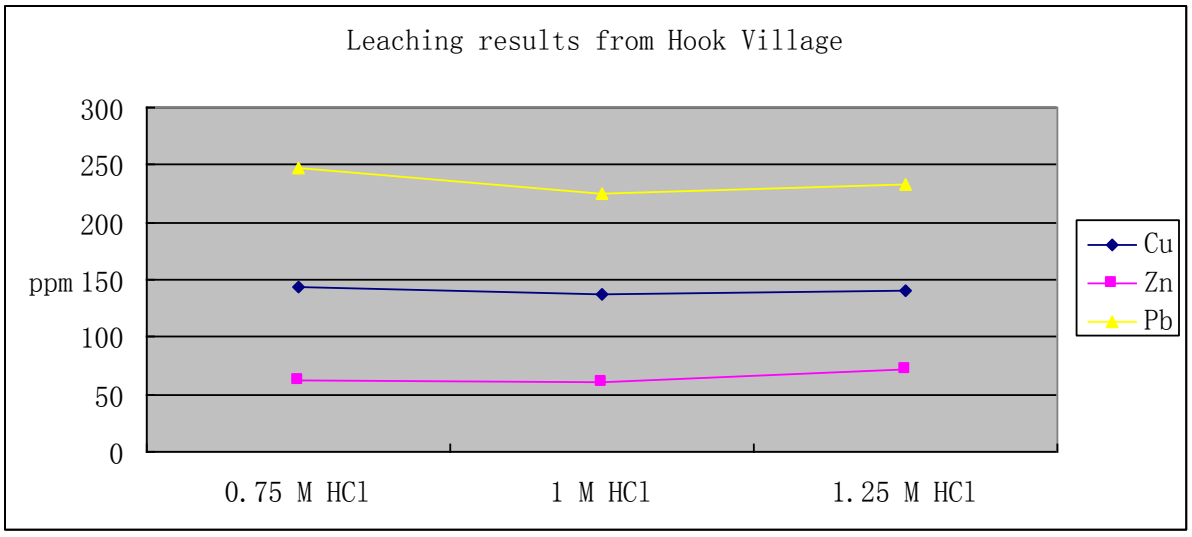


Figure 4.3.3 Trendlines of Cu, Zn, Pb Leached from Hook Village using three additional concentrations (0.75 M, 1 M and 1.25 M) of hydrochloric acid and detected by AAS

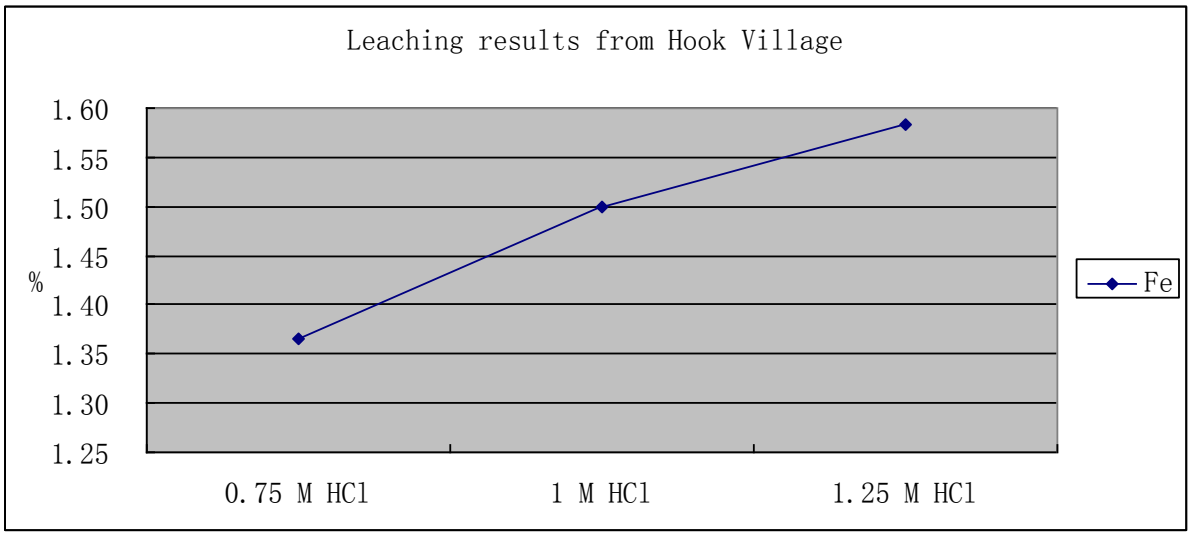


Figure 4.3.4 Trendline of Fe leached from Hook Village using three additional concentrations (0.75 M, 1 M and 1.25 M) of hydrochloric acid and detected by AAS

The data shown in Figure 4.3.3 and Figure 4.3.4 shows that for copper and lead, when the concentration of hydrochloric acid is more than 0.75 M, there is no further leaching of metal ions from the solution. And for zinc it changes very little. But for iron, the concentration is still increasing which may be because iron is the fourth most abundant element in the Earth's crust and there is a high concentration of iron in the soil samples analysed here.

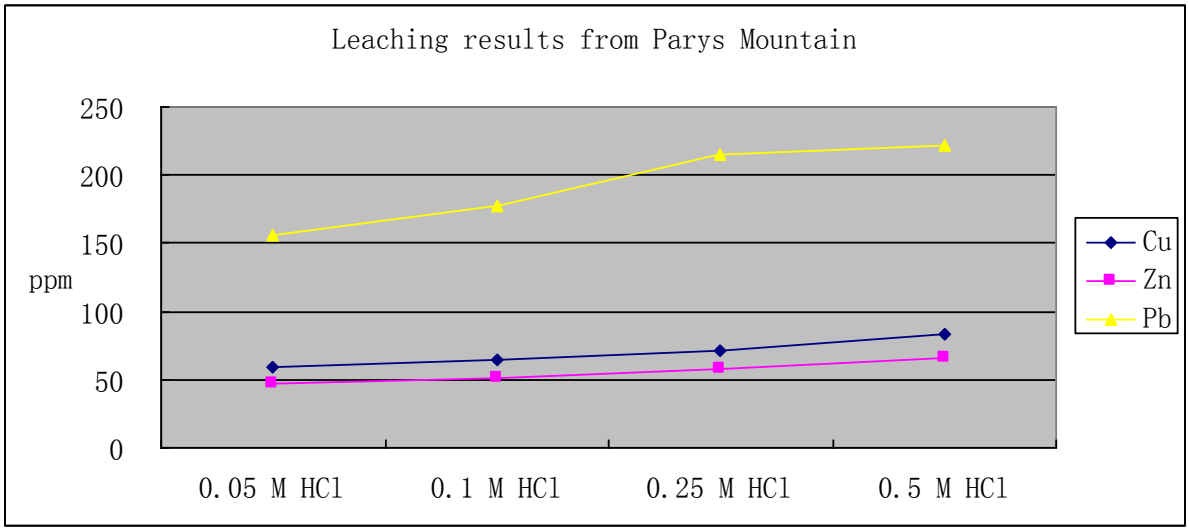


Figure 4.3.5 Trendlines of Cu, Zn, Pb Leached from Parys Mountain soil samples by using four different concentrations (0.05 M, 0.1 M, 0.25 M, 0.5 M) of hydrochloric acid and detected by AAS

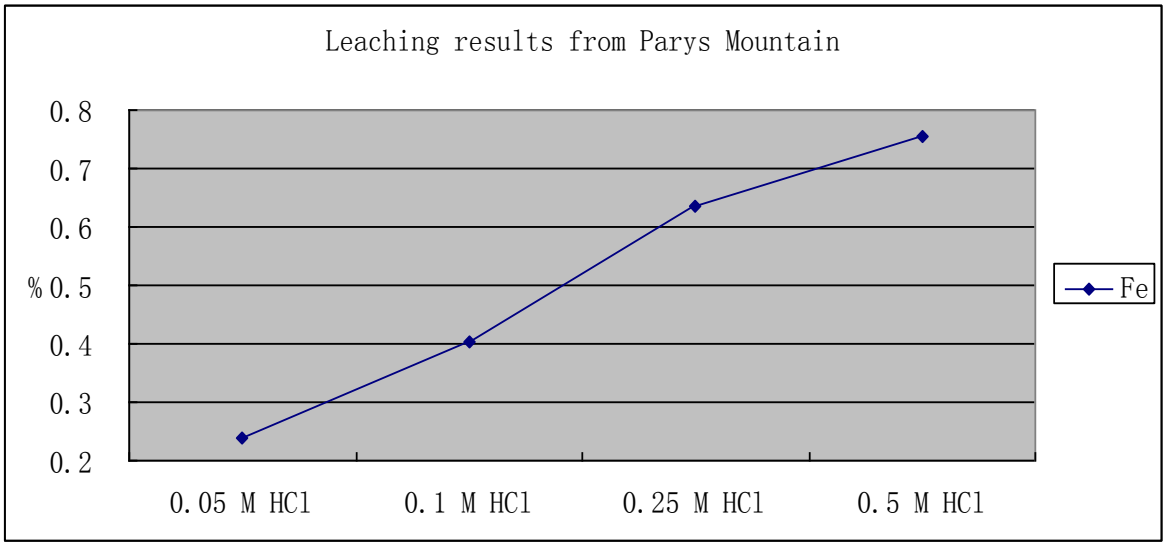


Figure 4.3.6 Trendline of Fe leached from Parys Mountain using four different concentrations (0.05 M, 0.1 M, 0.25 M, 0.5 M) of hydrochloric acid and detected by AAS

Table 4.3.2 Concentrations of Cu, Zn, Pb Leached from Parys Mountain soil samples by using four different concentrations (0.05 M, 0.1 M, 0.25 M, 0.5 M) of hydrochloric acid

HCl	Cu (ppm)	Zn (ppm)	Pb (ppm)	Fe %
0.05 M	59	47	156	0.24
0.1 M	64	52	178	0.40
0.25 M	71	58	214	0.64
0.5 M	83	66	222	0.75

From Figure 4.3.5 and Figure 4.3.6, it is easy to see when using HCl solution that the increase of HCl solution concentration leads to more metal ions being leached out. The leaching results tendency from Parys Mountain is similar to that of the soil samples from Hook Village. But the extraction rate from Parys Mountain had some differences with those from Hook Village. Comparing this result with XRF results, nearly 87% of the copper ion, 84 % of the lead ion, 64 % of the zinc ion and just 29 % of the iron ion have been extracted out. The tendency suggests that a higher concentration of HCl solution could be used to try to get a higher extraction.

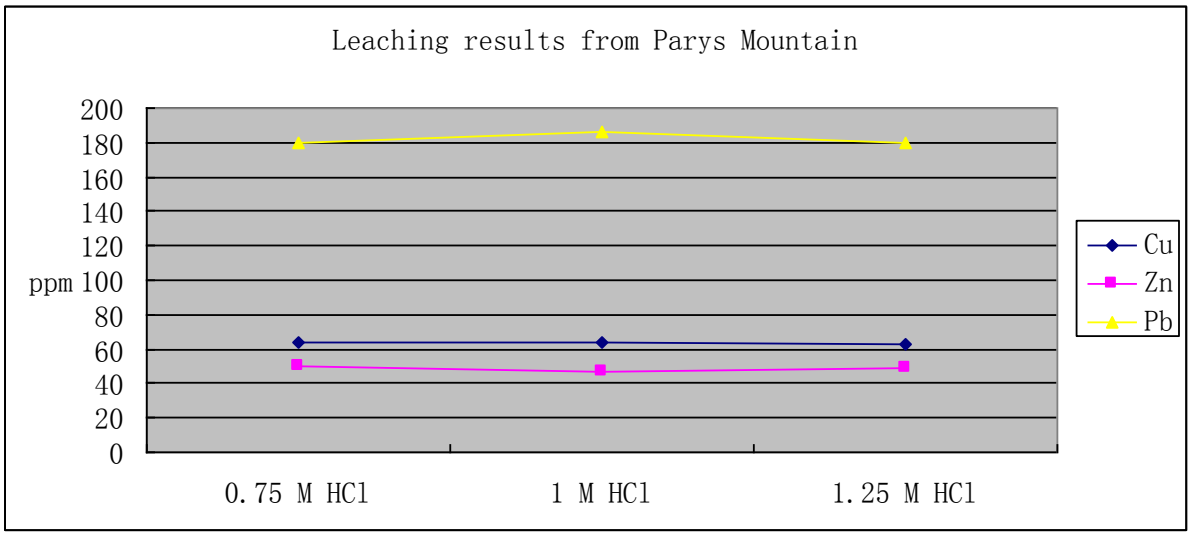


Figure 4.3.7 Trendlines of Cu, Zn and Pb leached from Parys Mountain using three additional concentrations (0.75 M, 1 M and 1.25 M) of hydrochloric acid and detected by AAS

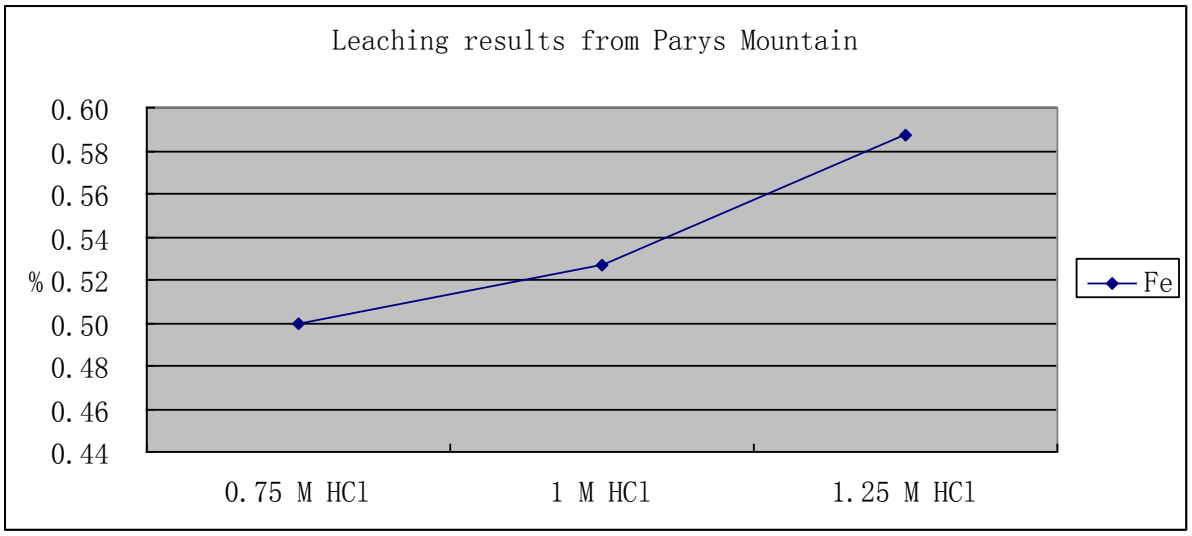


Figure 4.3.8 Trendline of Fe leached from Parys Mountain using three additional concentrations (0.75 M, 1 M and 1.25 M) of hydrochloric acid and detected by AAS

The data from Figure 4.3.7 and Figure 4.3.8 show that for copper, zinc and lead, even

when the concentration is more than 0.75 M, there is no further leaching of metal ions from the solution. It suggests for dilute hydrochloric acid, concentrations above 0.75 M HCl do not cause further leaching of these metals. For iron, by using leaching solutions with progressively increasing HCl concentrations (ranging from 0.75 to 1.25 M HCl), a gradient in the amount of iron leached out has been reached (Figure. 4.3.8) which may because there is a high concentration of iron in the soil samples analyzed here. These results illustrate an important general principle that where metals concentrations in the soil are higher, then higher concentrations of acid will continue to leach out a higher proportion of the metal.

4.4 Different concentrations of sulfuric acid (H_2SO_4)

When using H_2SO_4 as matrix, lead ions always gave interesting results. A wide range of different concentrations of sulfuric acid have been used as matrices to obtain a clear trend. And also increasing concentrations of acids have been used to find which concentration was best for leaching metals from soil.

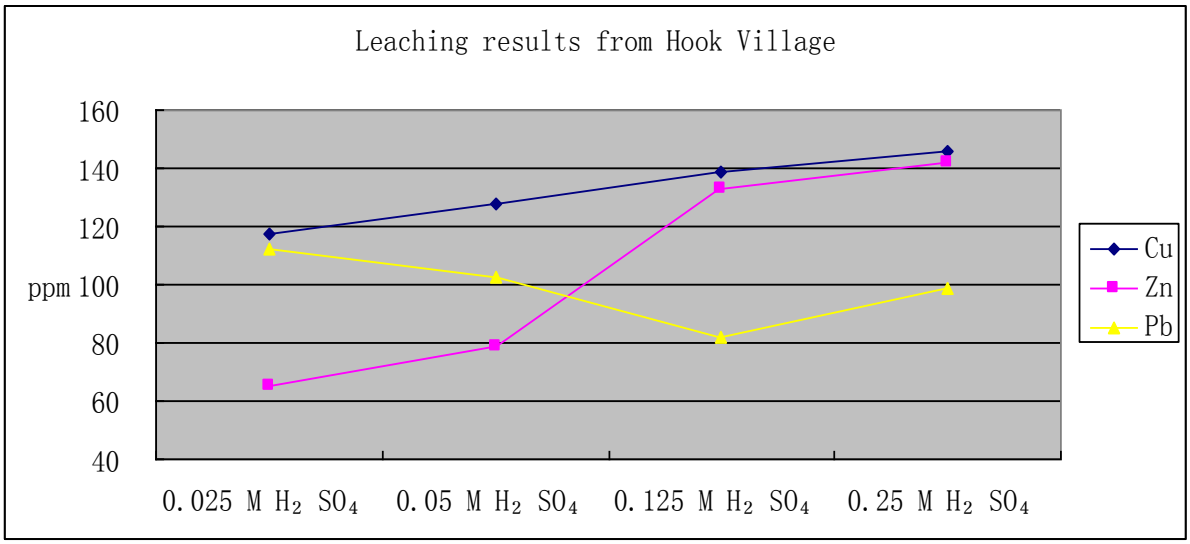


Figure 4.4.1 Trendlines of Cu, Zn, Pb Leached from Hook Village using four different concentrations (0.025 M, 0.05 M, 0.125 M, 0.25 M) of sulfuric acid and detected by AAS

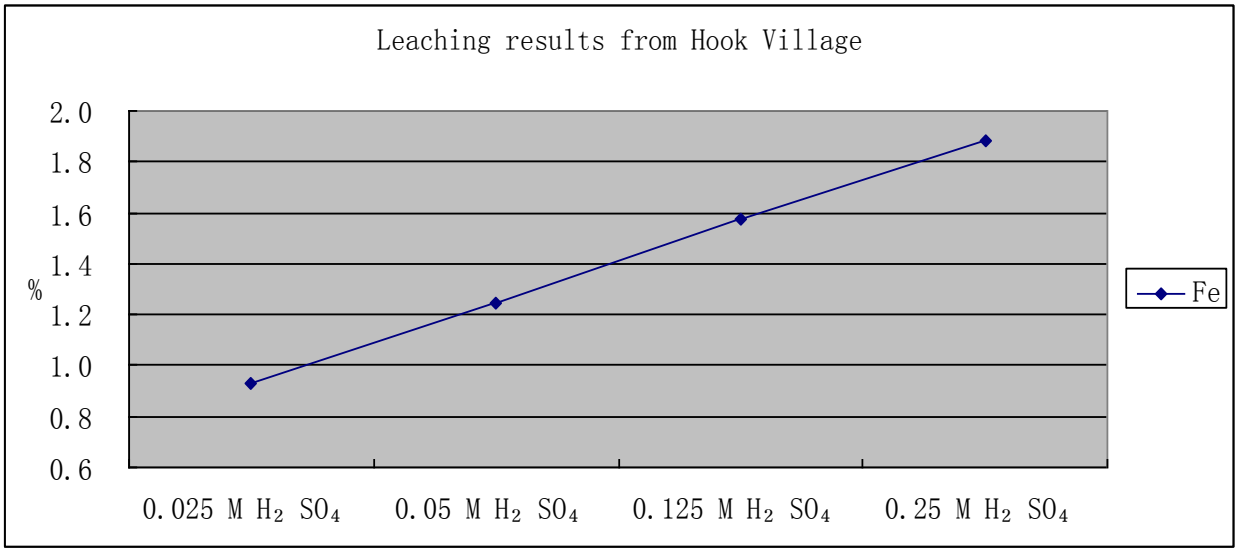


Figure 4.4.2 Trendline of Fe leached from Hook Village using four different concentrations (0.025 M, 0.05 M, 0.125 M, 0.25 M) of sulfuric acid and detected by AAS

Table 4.4.1 Concentrations of Cu, Zn, Pb Leached from Hook Village soil samples by using four different concentrations (0.025 M, 0.05 M, 0.125 M, 0.25 M) of sulfuric acid

H_2SO_4	Cu (ppm)	Zn (ppm)	Pb (ppm)	Fe %
0.025 M	117	65	112	0.93
0.05 M	127	79	103	1.25
0.125 M	139	133	82	1.58
0.25 M	146	142	99	1.88

Although the matrices are all inorganic acids, the results from HCl solution and H_2SO_4 solution are quite different. From the Figure 4.4.1 and Figure 4.4.2, they show when using H_2SO_4 solution that increasing H_2SO_4 solution concentration leads to more metal ions (Cu, Zn and Fe) being leached out. Comparing this result with XRF results, nearly 64% of the copper ion, 46 % of the zinc ion and 40 % of the iron ion have been extracted out which suggest that higher concentrations of H_2SO_4 solution could be used to try to get a higher extraction of metals. The total extraction of metals leached by H_2SO_4 solution is less than that with HCl solution. The reason may be that different solubility of salts may affect the leaching results. It will be discussed in section 4.7. But lead shows a different curve which may be because the solubility of $PbSO_4$ (very slightly soluble in water, 42.5 mg / L at 25 °C) is quite different from that of $PbCl_2$ (partially soluble in cold water 9.9 g / L at 20 °C [23]).

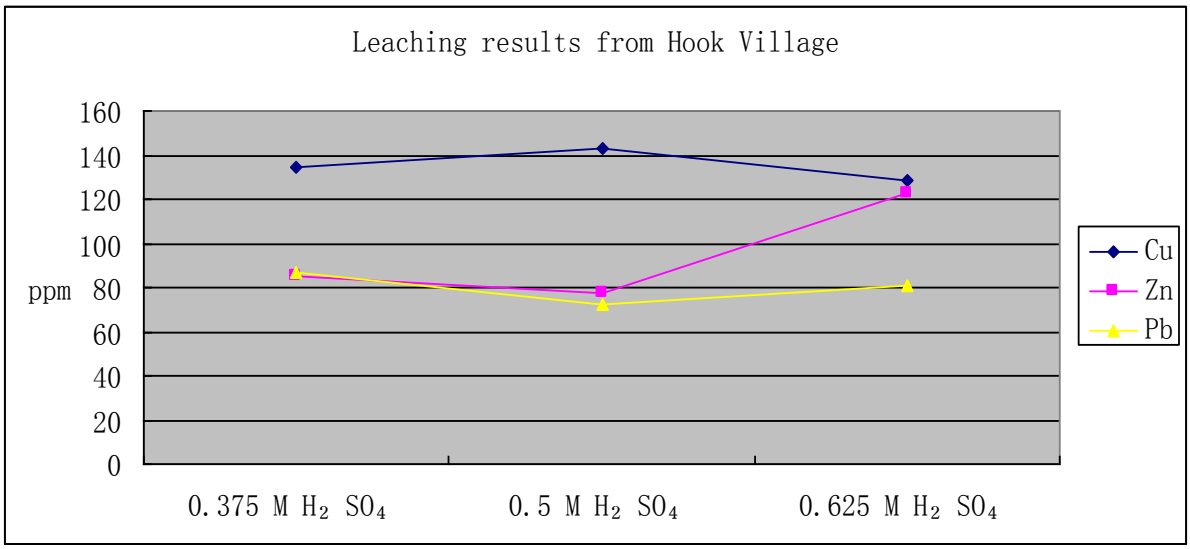


Figure 4.4.3 Trendlines of Cu, Zn, Pb Leached from Hook Village using three additional concentrations (0.375 M, 0.5 M, 0.625 M) of sulfuric acid and detected by AAS

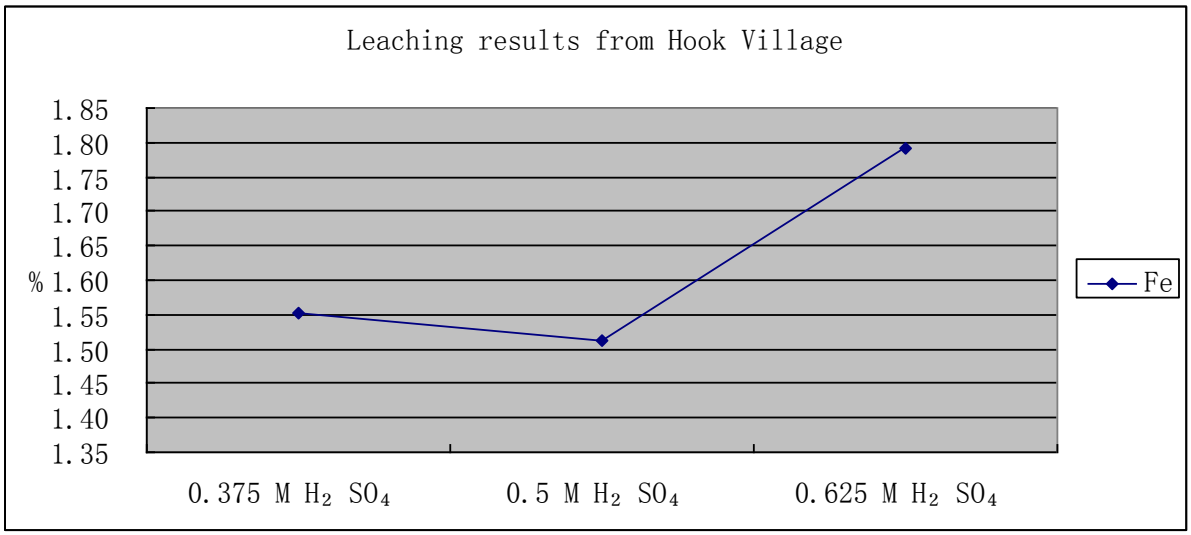


Figure 4.4.4 Trendline of Fe Leached from Hook Village using three additional concentrations (0.375 M, 0.5 M, 0.625 M) of sulfuric acid and detected by AAS

The data shown in Figure 4.4.3 and Figure 4.4.4 shows that for copper and lead, when the

concentration of sulfuric acid is more than 0.375 M, there is no further leaching of metal ions from the solution. But for zinc, when the concentration of sulfuric acid is increased from 0.5 M to 0.625 M, the concentration of metal extracted increases from 77.5 ppm to 122.9 ppm. This is an unexpected result as it increased so rapidly. The repeat experiment shows that when using 0.625 M H_2SO_4 solution, 83.41 ppm of Zinc has been leached out. Comparing the results with using 0.375 H_2SO_4 M (85.22 ppm) in Figure 4.4.3, that there is little change in the amount of metal extracted. This suggests that the original result of 122.9 ppm obtained with 0.625 M H_2SO_4 was probably an outlier. It is noteworthy that 0.5 M H_2SO_4 leaches out less iron than does 0.375 M H_2SO_4. In Figure 4.4.4, the point for 0.5 M H_2SO_4 (1.51 %) is an average of four repeating values which were found to include an outlier (detail can be check in chapter 3.3.3). So the updated figure with the outlier removed is given below:

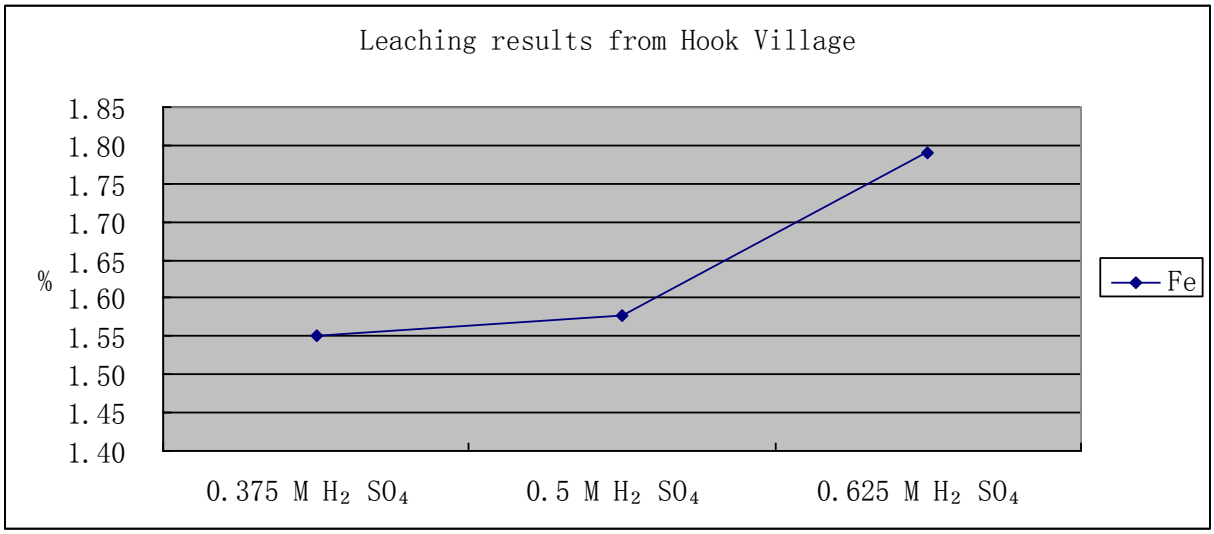


Figure 4.4.5 Trendline of Fe Leached from Hook Village using three additional concentrations (0.375 M, 0.5 M, 0.625 M) of sulfuric acid and detected by AAS

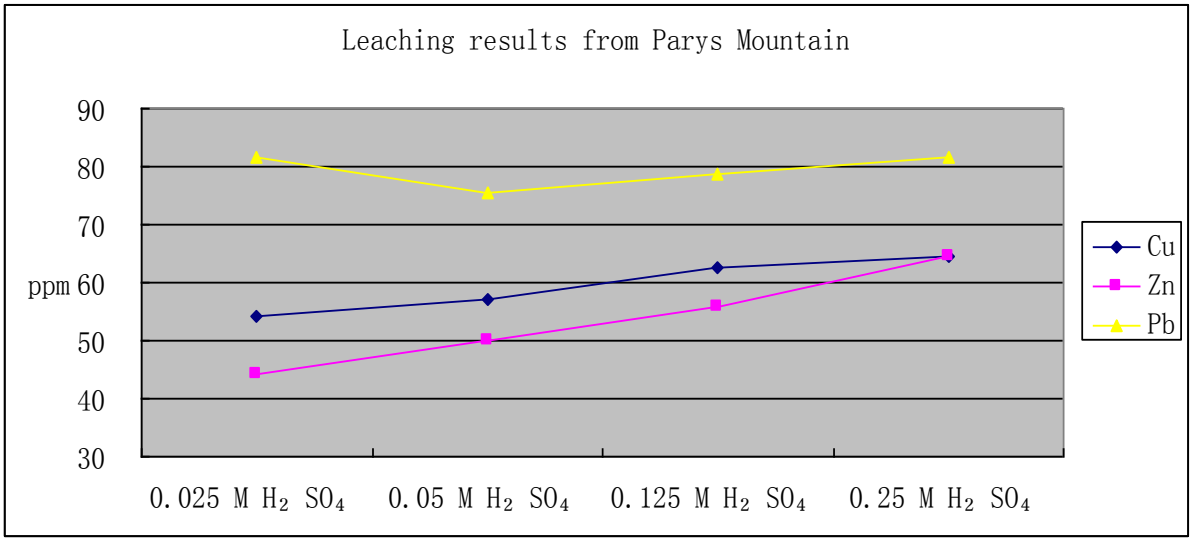


Figure 4.4.6 Trendlines of Cu, Zn, Pb Leached from Parys Mountain using four different concentrations (0.025 M, 0.05 M, 0.125 M, 0.25 M) of sulfuric acid and detected by AAS

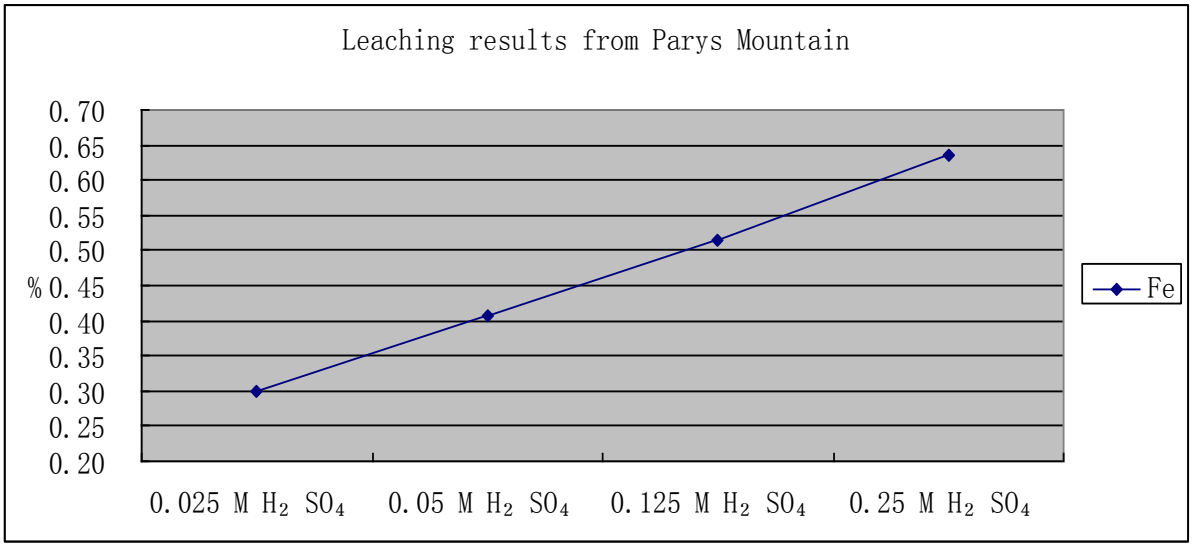


Figure 4.4.7 Trendiline of Fe Leached from Parys Mountain using four different concentrations (0.025 M, 0.05 M, 0.125 M, 0.25 M) of sulfuric acid and detected by AAS

Table 4.4.3 Concentrations of Cu, Zn, Pb Leached from Parys mountain soil samples by using four different concentrations (0.025 M, 0.05 M, 0.125 M, 0.25 M) of sulfuric acid

H_2SO_4	Cu (ppm)	Zn (ppm)	Pb (ppm)	Fe %
0.025 M	54	44	82	0.30
0.05 M	57	50	75	0.41
0.125 M	63	56	79	0.52
0.25 M	64	65	82	0.63

From the data above it shows that when using H_2SO_4 solution that increasing the H_2SO_4 solution concentration leads to more metal ions (copper, zinc and iron) being leached out. Comparing this result with XRF results, shows that nearly 67% of the copper ion, and 25 % of the iron ion have been extracted out which suggests that higher concentrations of H_2SO_4 solution can be used to try to get a higher extraction. But lead shows a different curve. Further discussion about lead will be given in a later section of this thesis.

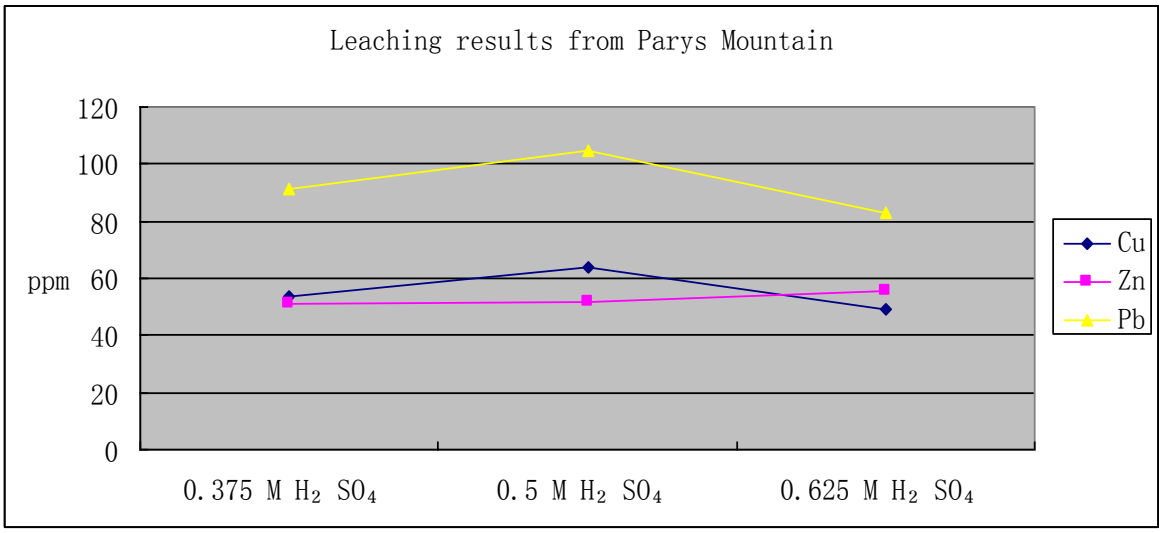


Figure 4.4.8 Trendlines of Cu, Zn, Pb Leached from Parys Mountain using three additional concentrations (0.375 M, 0.5 M, 0.625 M) of sulfuric acid and detected by AAS

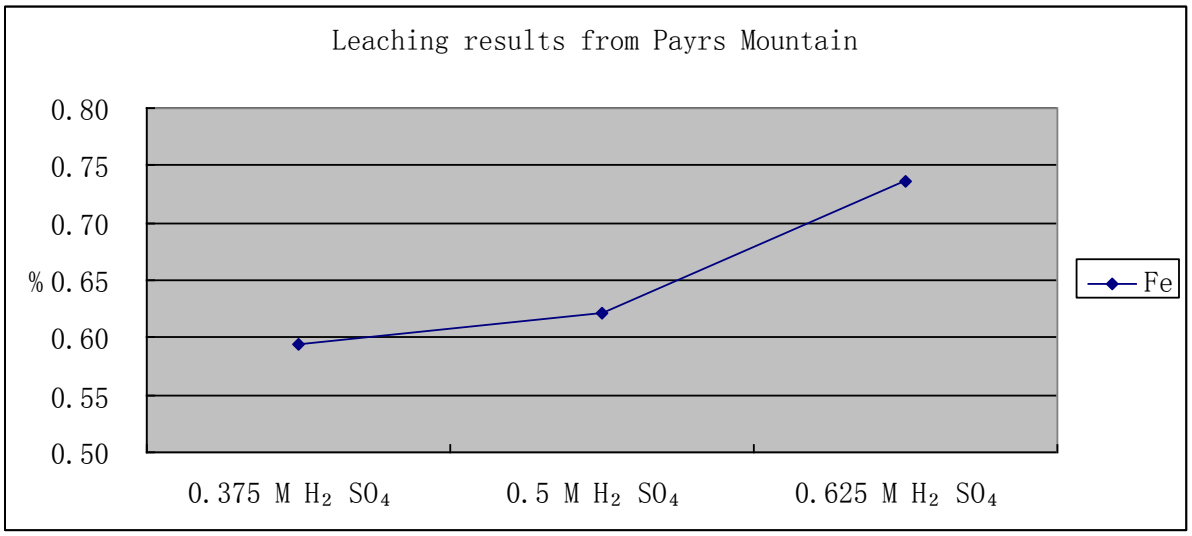


Figure 4.4.9 Trendline of Fe Leached from Parys Mountain using three additional concentrations (0.375 M, 0.5 M, 0.625 M) of sulfuric acid and detected by AAS

Figure 4.4.8 and Figure 4.4.9 show that for copper and lead, when the concentration of sulfuric acid is more than 0.5 M, there is no further leaching of metal ions from the solution. For copper, when using 0.625 M H_2SO_4 solution as matrix, a small decrease in the concentration of the leachate is seen. And for zinc there is a slight increase (from 51 ppm with 0.375 M H_2SO_4 to 55 ppm with 0.625 M H_2SO_4). Also for iron, the amount of leached metal is still increasing which may because of the high iron content in soil.

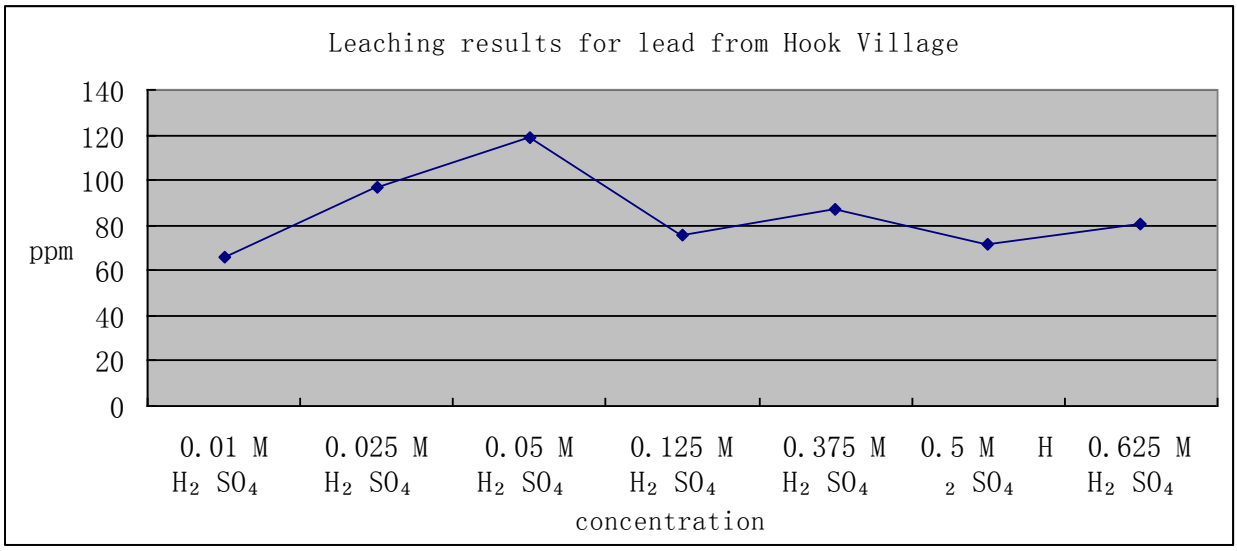


Figure 4.4.10 the amount of Pb leached from Hook Village using seven different concentrations (0.01 M, 0.025 M, 0.05 M, 0.125 M, 0.375 M, 0.5 M, 0.625 M) of sulfuric acid and detected by AAS

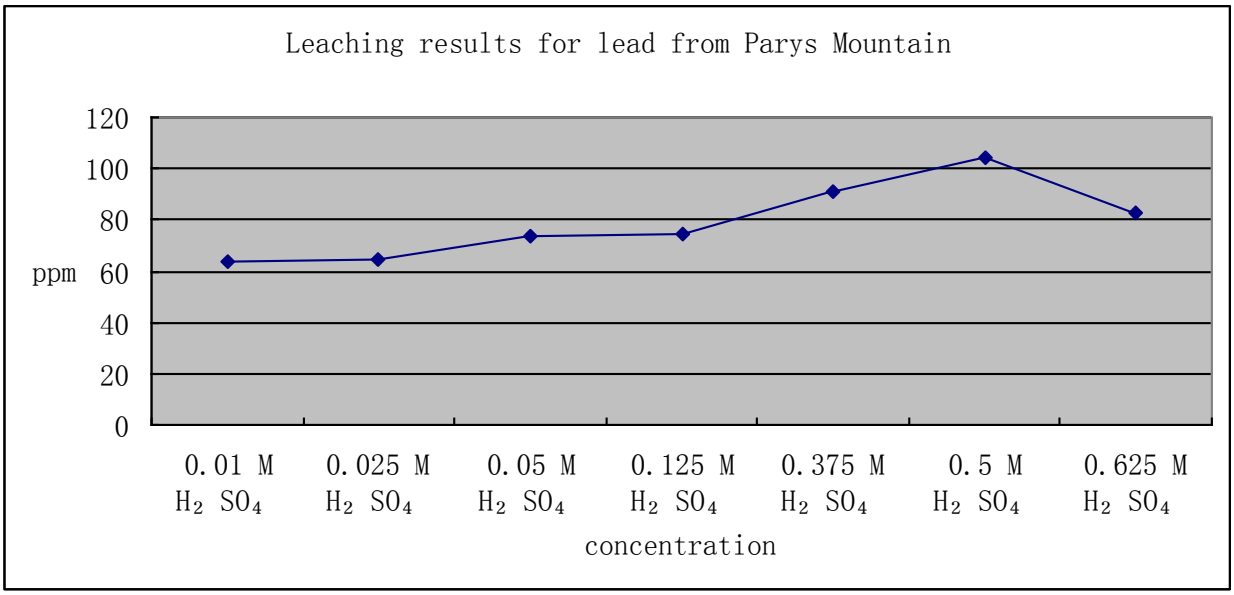


Figure 4.4.11 the amount of Pb leached from Parys mountain using seven different concentrations (0.01 M, 0.025 M, 0.05 M, 0.125 M, 0.375 M, 0.5 M, 0.625 M) of sulfuric acid and detected by AAS

As lead shows a different curve in Figure 4.4.1 and Figure 4.4.6, progressively increasing concentrations of sulfuric acid have been used to investigate further. The leaching results for lead are quite different when using HCl and H_2SO_4 solution which may be because lead sulfate ($PbSO_4$) is very slightly soluble in water (42.5 mg / L at 25 °C) while lead chloride ($PbCl_2$) is partially soluble. When changing the concentration of sulfuric acid, the following reaction will happen:

$$H_2SO_4\,(aq) \leftrightharpoons HSO_4^-\,(aq) + H^+\,(aq) \leftrightharpoons SO4^{2-}\,(aq) + 2H^+\,(aq)$$

$$Pb^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow PbSO_4\,(s)$$

$PbSO_4$ is very slightly soluble in water, slightly soluble in dilute sulfuric acid, more soluble in concentrated sulfuric acid [23]. When the concentration of sulfuric acid is increasing, the H^+ is also increasing which may enhance the solubility of the lead compound. But at the same time, the amount of SO_4^{2-} also increased which may lead to more $PbSO_4$ precipitation. It may therefore reduce the solubility of lead ions. The two effects added together may produce the curve above which shows no clear trend.

Although the leaching results for lead from two sites both give curves with no clear trend, a comparison of the two figures shows that the soil samples from Hook Village leached the most lead when using 0.05 M H_2SO_4 solution as matrix. But for the samples from Parys Mountain, the peak is at 0.5 M H_2SO_4 solution. One reason may be that soils from two sites have different acidity. The samples from Hook village are more acidic as the pH value is 5.79 while the samples from Parys Mountain are weakly alkaline with a pH value of nearly 7.42. Another reason may be the lead ions in the two sites are found in different chemical components such as galena (PbS), anglesite ($PbSO_4$), minium (Pb_3O_4) and cerussite ($PbCO_3$). Pb compounds in soil are speciated in different ways, with different solubilities [23]. For instance, it is difficult to release Pb^{2+} ions from PbS in both acid solution and alkaline solution while $PbCO_3$ can dissolve in alkaline solution. In previous studies [24], powder-X-ray diffraction has been done to attempt to determine the

composition of the soil samples. But the results showed that highly crystalline materials such as quartz will dominate a powder XRD pattern while poorly-crystalline clay minerals or minor components such as lead salts will only give weak features. Powder-XRD cannot clearly show which mineral is present in the soil because they are at too low a concentration.

4.5 Different concentrations of Nitric acid (HNO_3)

Dilute HNO_3 solutions were also used as matrices and increasing concentrations of acids have been used to find which concentration was best for leaching metals from soil. As iron is the fourth most abundant element in the Earth's crust, there is too much iron in the soil sample. From step 4.3 and 4.4 it is easy to find that the amount of iron leached from the soil keeps increasing when the concentration of the acids increases. Here are shown only the leaching results of copper, lead and zinc.

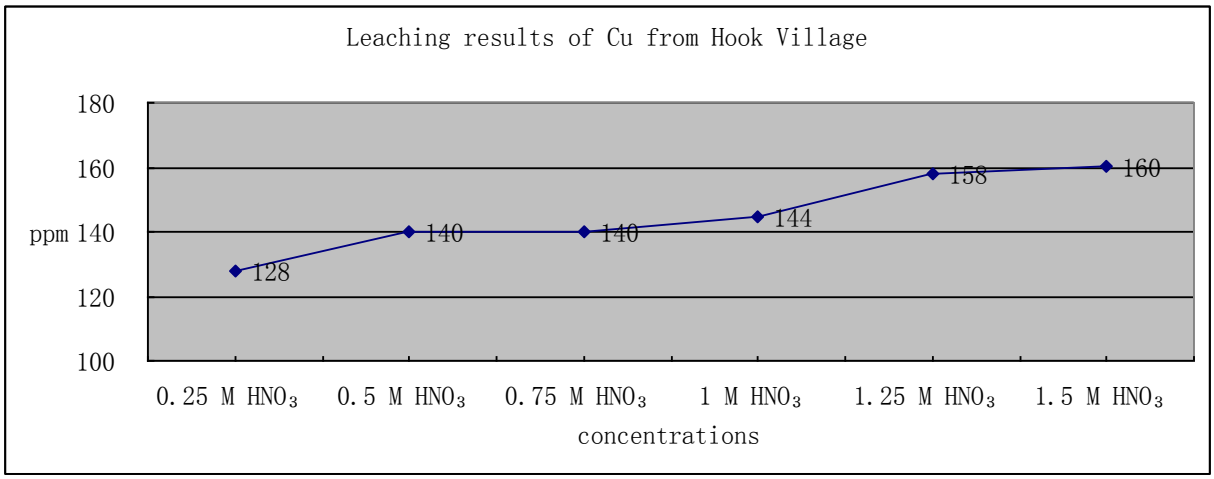


Figure 4.5.1 Trend line of Cu Leached from Hook Village soil samples by using six different concentrations (0.25 M, 0.5 M, 0.75M, 1 M, 1.25 M, 1.5 M) of nitric acid and detected by AAS

From the Figure 4.5.1 it is shown for the soil samples from Hook Village, when using HNO_3 solution that the increase of HNO_3 solution concentration leads to more copper ions being leached out. And comparing this result with XRF results, 71% of the copper ion has been extracted out at a concentration of 1.5 M HNO_3. Also it shows when using 0.5 M HNO_3 and 0.75 M HNO_3 as matrices that the amount of metal leached does not increase. But when the concentrations of nitric acid keep increasing, more copper ions have been leached out. The leaching result for copper in 1.25 M HNO_3 solution is 158 ppm while in 1.5 M HNO_3 solution it is 160 ppm. The results are quite close to each other which shows that maybe above 1.5 M HNO_3 no further leaching takes place.

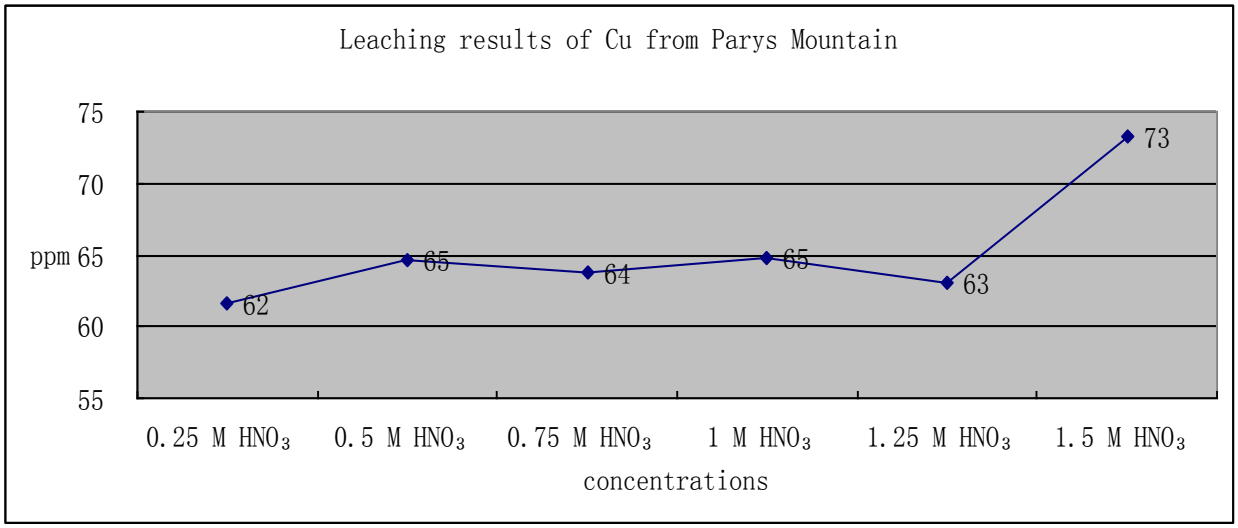


Figure 4.5.2 Trend line of Cu Leached from Parys Mountain soil samples by using six different concentrations (0.25 M, 0.5 M, 0.75M, 1 M, 1.25 M, 1.5 M) of nitric acid and detected by AAS

Figure 4.5.2 shows an interesting trend line of copper from Parys Mountain when using different concentrations of nitric acid as matrices. It is easy to find that the increasing of HNO_3 solution concentration (from 0.25M to 1.25 M) does not lead to more copper being leached out. But when using 1.5 M HNO_3 as matrix, a rapid increase of leaching results

appears (from 63ppm to 73ppm). Statistical analysis of the data has shown that the result using 1.5 M HNO_3 is "real" result and is not simply an outlier. a Comparing this result with XRF results, when the concentrations of nitric acid increase from 0.25 M to 1.25 M, nearly 67% of the copper ions have been extracted out. But 76 % of the copper ions have been extracted out when using 1.5 M nitric acid as matrix.

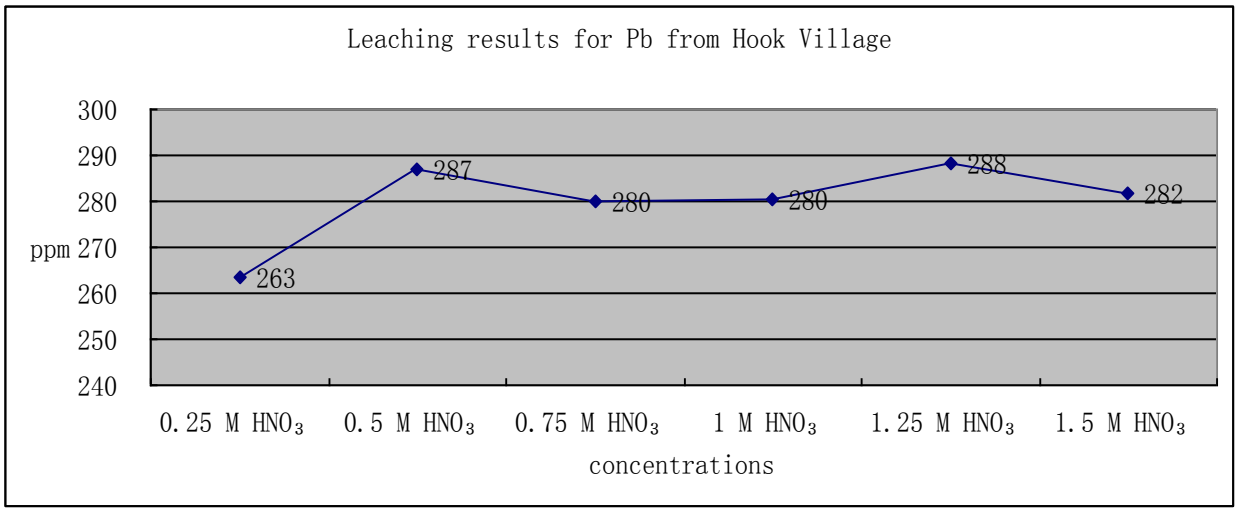


Figure 4.5.3 Trend line of Pb Leached from Hook Village soil samples by using six different concentrations (0.25 M, 0.5 M, 0.75M, 1 M, 1.25 M, 1.5 M) of nitric acid and detected by AAS

Figure 4.5.3 shows a trend line of lead for the soil samples from Hook Village when using different concentrations of nitric acid as matrices. The amount of Pb leached out from 0.25 M HNO_3 to 0.5 M HNO_3 increases rapidly (263ppm to 287 ppm). But when the concentrations of nitric acid keep increasing, there is no more Pb that has been extracted out. It means that 0.5 M HNO_3 is strong enough to extract out all the extractable Pb from soil samples from Hook Village. And comparing this result with XRF results, 76% of the Pb ions have been extracted out.

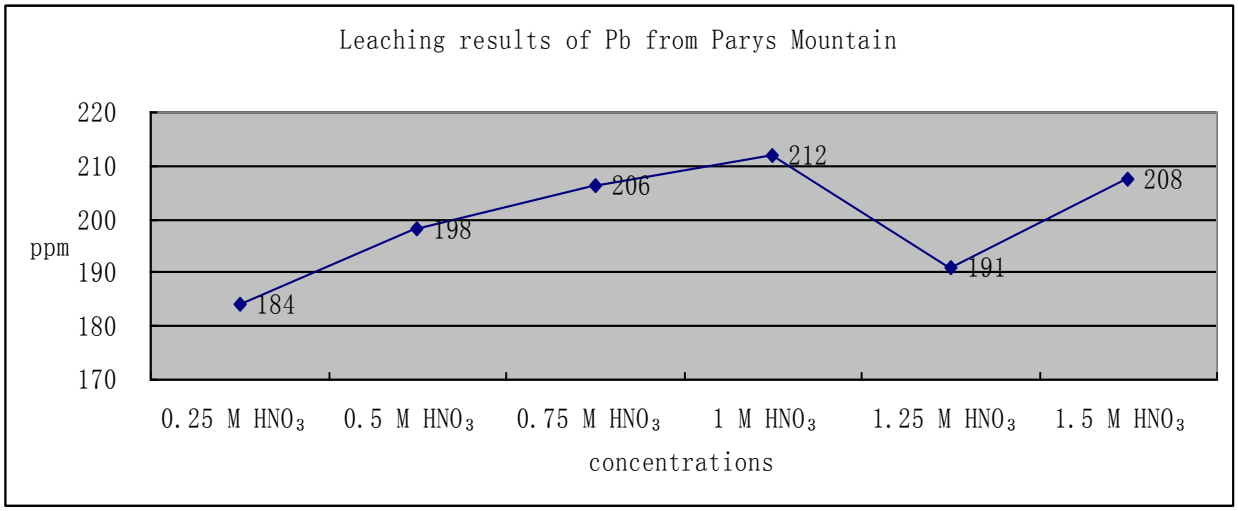


Figure 4.5.4 Trend line of Pb Leached from Parys Mountain soil samples by using six different concentrations (0.25 M, 0.5 M, 0.75M, 1 M, 1.25 M, 1.5 M) of nitric acid and detected by AAS

From Figure 4.5.4 it is shown for the soil samples from Parys Mountain, when using HNO_3 solution as matrices that the increase of HNO_3 solution concentration (0.25 M to 1 M) leads to more copper ions being leached out and comparing this result with XRF results, 80 % of the Cu ions have been extracted out when using 1 M nitric acid as matrix. When using 1.25 M HNO_3 as matrix, there is a value lower than the other leaching results but when using 1.5 M HNO_3 as matrix, the leaching results are still close to the results of 1M HNO_3. The low value may come from outliers as the soil samples are never homogenous and fewer repeat experiments have been done (see Figure 4.5.5). The procedure for rejection of outliers has been described in chapter 3.

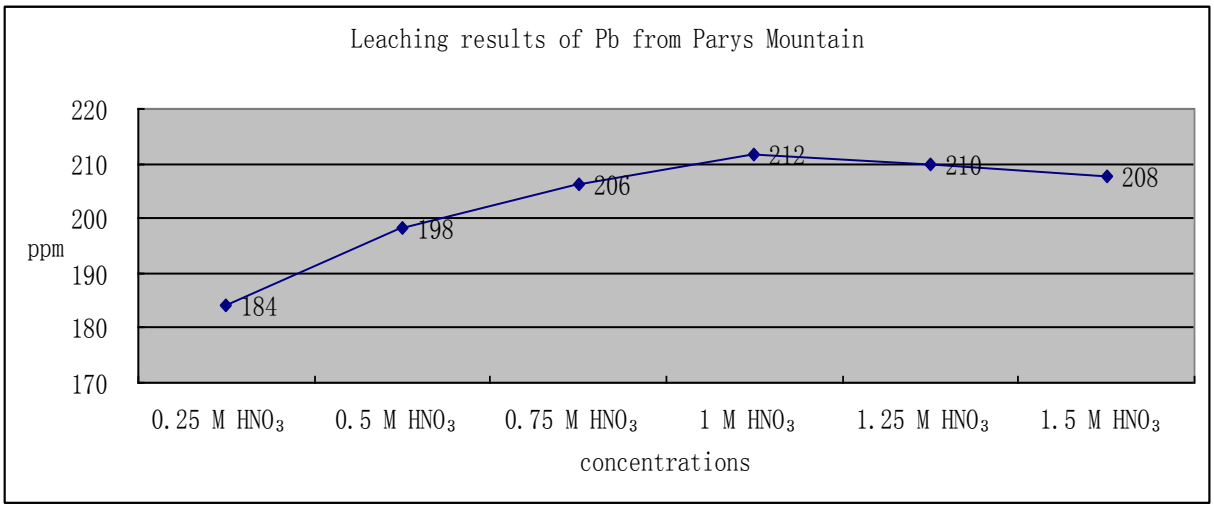


Figure 4.5.5 Trend line of Pb Leached from Parys Mountain soil samples by using six different concentrations (0.25 M, 0.5 M, 0.75M, 1 M, 1.25 M, 1.5 M) of nitric acid and detected by AAS

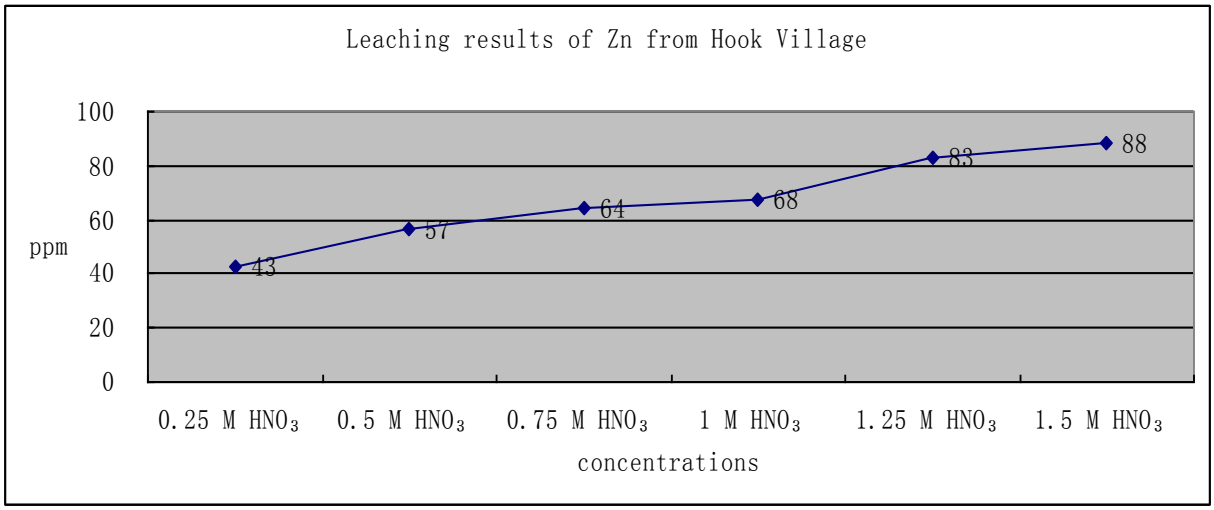


Figure 4.5.6 Trend line of Zn Leached from Hook Village soil samples by using six different concentrations (0.25 M, 0.5 M, 0.75M, 1 M, 1.25 M, 1.5 M) of nitric acid and detected by AAS

From the Figure 4.5.6, it is shown that for the soil samples from Hook Village, when using HNO_3 solution as matrices that the increase of HNO_3 solution concentration leads to more zinc ions being leached out. And comparing this result with XRF results, 28 % of the zinc ions have been extracted out with 1.5 M HNO_3. The leaching result for zinc in 1.25 M HNO_3 solution is 83 ppm while in 1.5 M HNO_3 solution it is 88 ppm. The results are quite close to each other which shows that 1.5 M HNO_3 solution is enough to remove all of the leachable Zn.

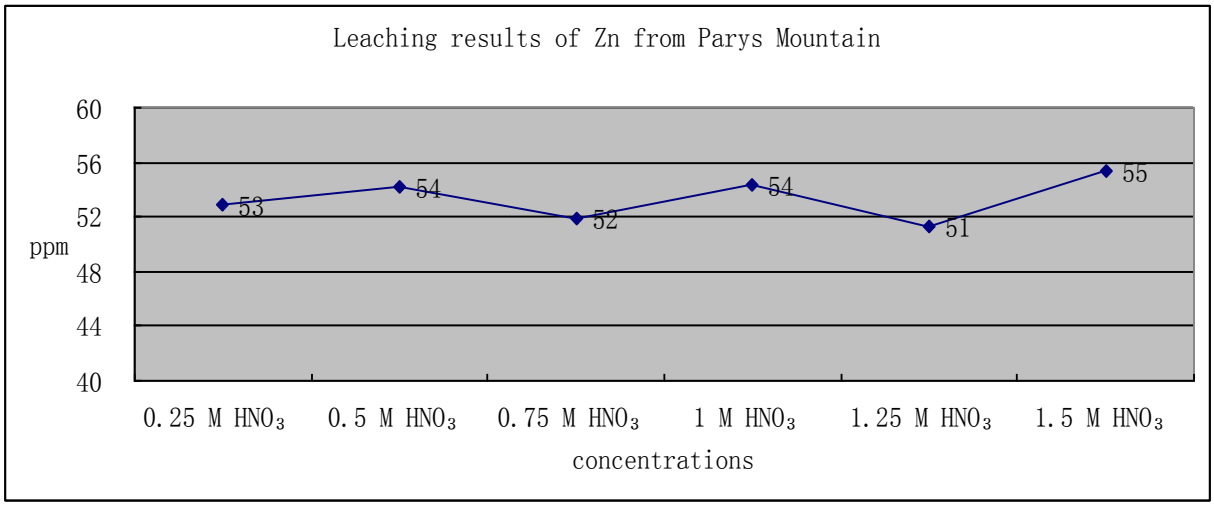


Figure 4.5.7 Trend line of Zn Leached from Parys Mountain soil samples by using six different concentrations (0.25 M, 0.5 M, 0.75M, 1 M, 1.25 M, 1.5 M) of nitric acid and detected by AAS

Figure 4.5.7 shows a curve of zinc from Parys Mountain when using different concentrations of nitric acid as matrices. The leaching results from six different concentrations of nitric acid are quite similar to each other. And comparing this result with XRF results, 53% of the Zn ions have been extracted out. This suggests that when using 0.25 M HNO_3 solution as matrices, all the extractable zinc has already leached out and even if the matrices are made more acidic it does not affect the leaching results.

4.6 Spiking experiments

Figure 4.4.10 and Figure 4.4.11 show a curve of leaching results for Pb when using different concentrations of H_2SO_4 solution. In this section are shown some further studies of "spiking" experiments to investigate the effect of adding additional SO_4^{2-} for leaching experiments. In the "spiking" experiments, different sulfate compounds and different amounts of sulfate were added to the original soil samples. Leaching experiments were carried out with the spiked samples to check whether the additional sulfate affects the leaching results. In this step, $CaSO_4$ (slightly soluble 2.4 g / L at 25 °C) and Na_2SO_4 (soluble 19.2 g / 100 mL at 20 °C) were selected as examples of sulfate compounds to study. The percentage of SO_4^{2-} ion in $CaSO_4$ is nearly 70 % while the percentage of SO_4^{2-} ion in Na_2SO_4 is 68 %. The two percentage values are close to each other.

4.6.1 Addition of different amounts of $CaSO_4$ to soil samples and leaching by H_2SO_4

The soil samples from Hook Village and Parys Mountain were taken and to them were added different amounts of $CaSO_4$ and then leaching was carried out using 20 mL 0.5 M H_2SO_4 solution to get a comparison. To the samples from each site were added 8 %, 12 % and 16 % of $CaSO_4$ respectively.

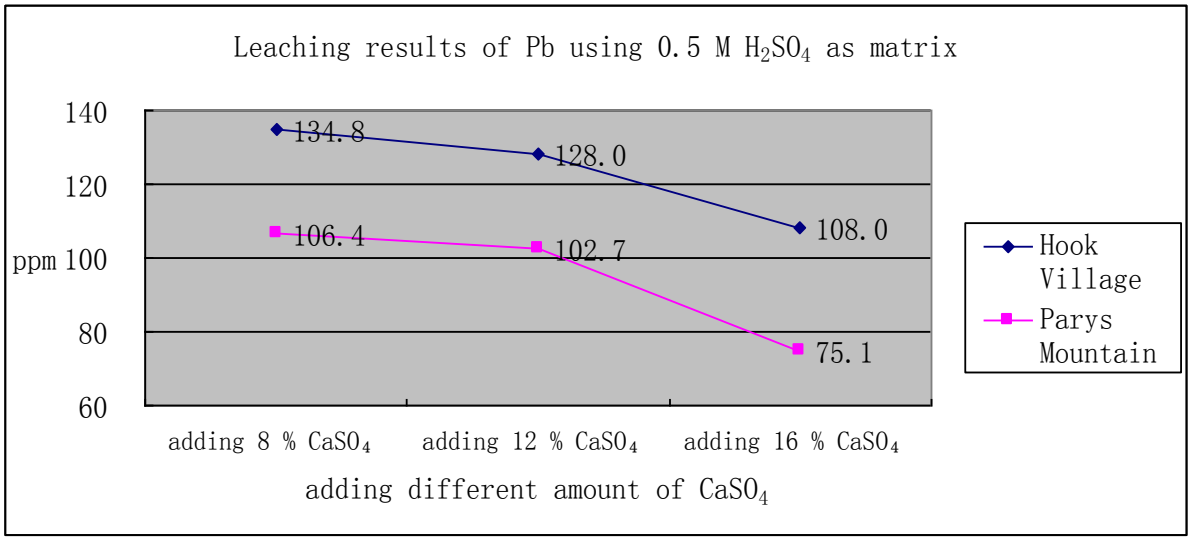


Figure 4.6.1 Trend lines of spike experiment to determine the concentration of Pb leached adding different amount of $CaSO_4$ (8 %, 12 % and 16 %) by 0.5 M H_2SO_4 from Hook Village and Parys Mountain and detected by AAS

From Figure 4.6.1, it is clear to find from both sites, that the more $CaSO_4$ is added into the soil samples, the less Pb ions can be leached out.

When using H_2SO_4 as matrices, the relevant equations are:

$H_2SO_4(aq) \leftrightharpoons HSO_4^-(aq) + H^+(aq)$,

$HSO_4^-(aq) \leftrightharpoons SO_4^{2-}(aq) + H^+(aq)$,

$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

In this spiking experiment, as more $CaSO_4$ is added into the solution, the third equation was promoted and more Pb precipitation appears. So less Pb ions can be extracted out.

4.6.2 Addition of different amounts of Na_2SO_4 to soil samples and leaching by H_2SO_4

Na_2SO_4 is more much soluble than $CaSO_4$. Here different amounts of Na_2SO_4 were added to soil samples which were leached by 20 mL 0.5 M H_2SO_4 solution. To the soil samples from Hook Village and Parys Mountain were added 8 %, 12 % and 16 % of Na_2SO_4 respectively.

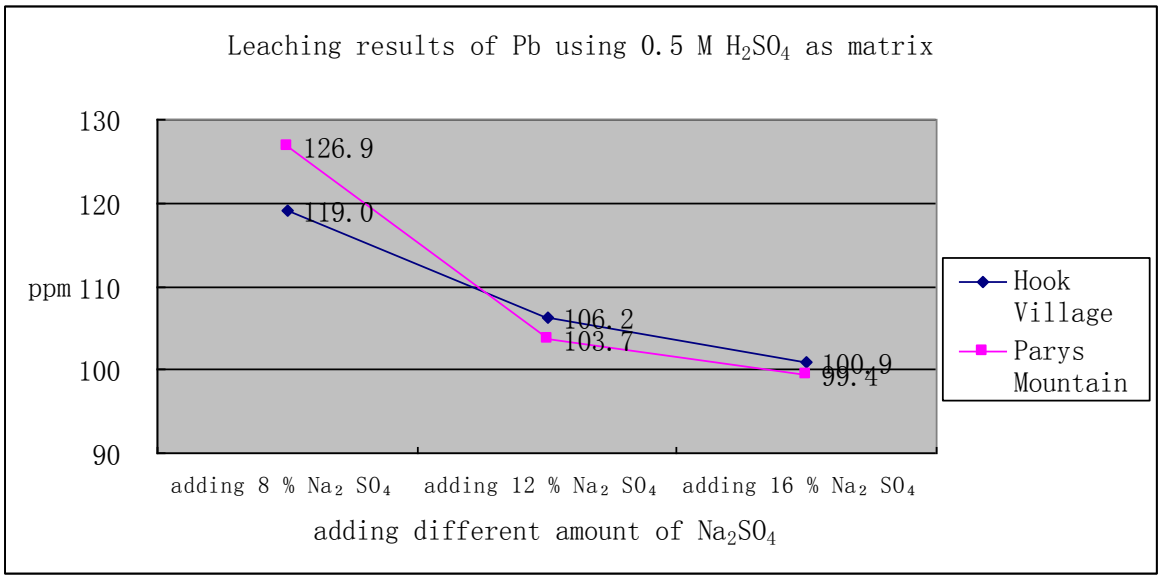
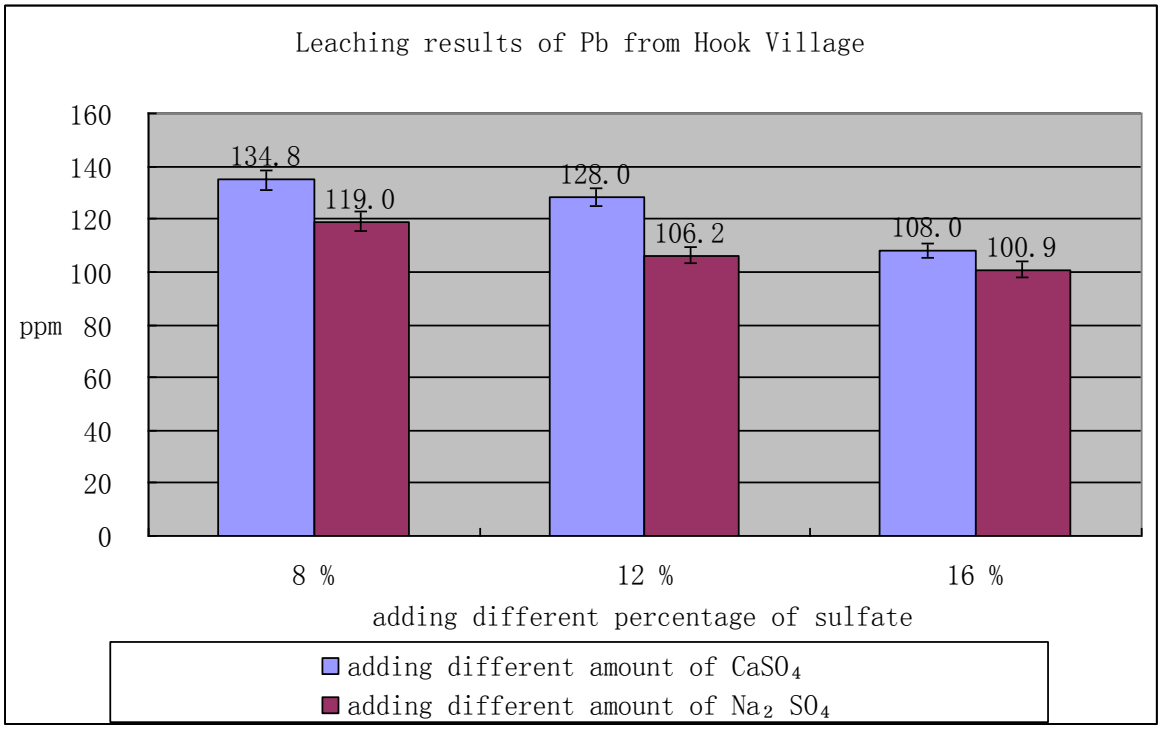
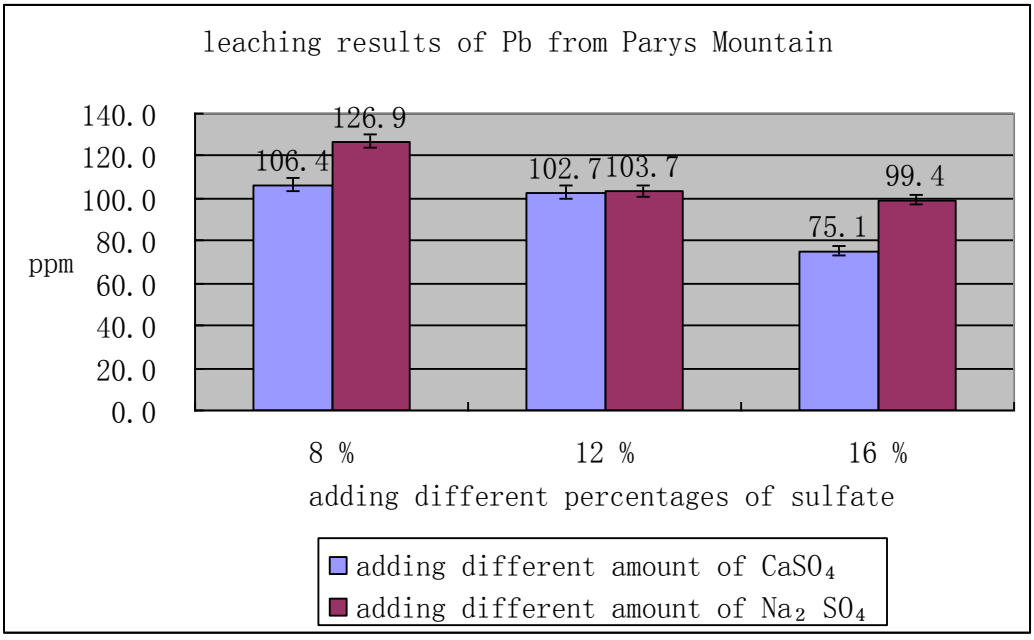


Figure 4.6.2.1 Trend lines of spiking experiments to determine the concentration of Pb leached out with adding different amount of Na_2SO_4 (8 %, 12 % and 16 %) by 0.5 M H_2SO_4 from Hook Village and Parys Mountain and detected by AAS

Figure 4.6.2.1 is quite similar to Figure 4.6.1. It is easy to find for the soil samples from Hook Village and Parys Mountain, the more Na_2SO_4 added into the soil samples, the less Pb ions can be leached out.



Figrue 4.6.2.2 Comparison of spiking experiments to determine the concentration of Pb leached by 0.5 M H_2SO_4 while adding different amount of $CaSO_4$ (8 %, 12 % and 16 %) and Na_2SO_4 (8 %, 12 % and 16 %) from Hook Village and detected by AAS

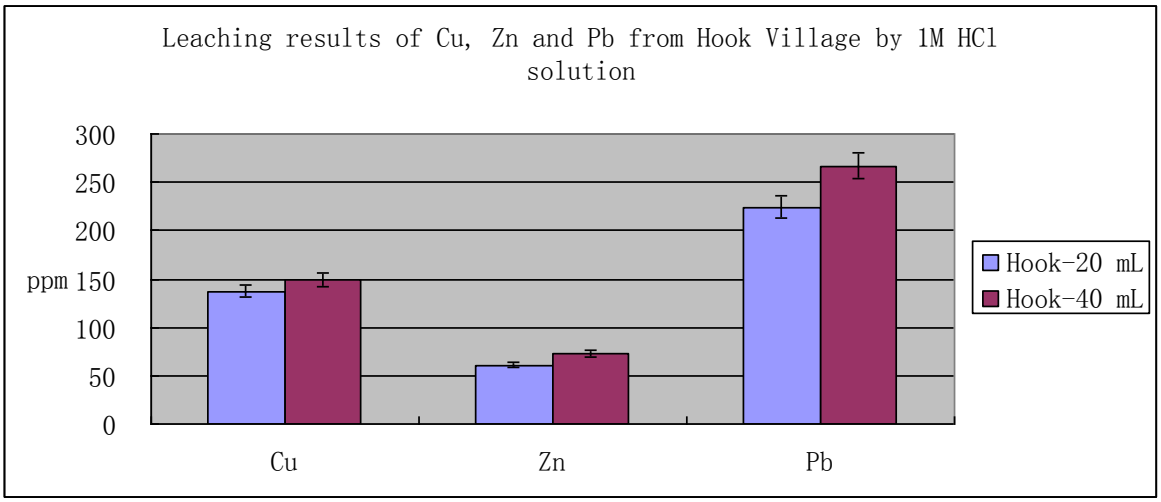


Figrue 4.6.2.3 Comparison of spiking experiments to determine the concentration of Pb leached by 0.5 M H_2SO_4 while adding different amount of $CaSO_4$ (8 %, 12 % and 16 %) and Na_2SO_4 (8 %, 12 % and 16 %) from Parys Mountain and detected by AAS

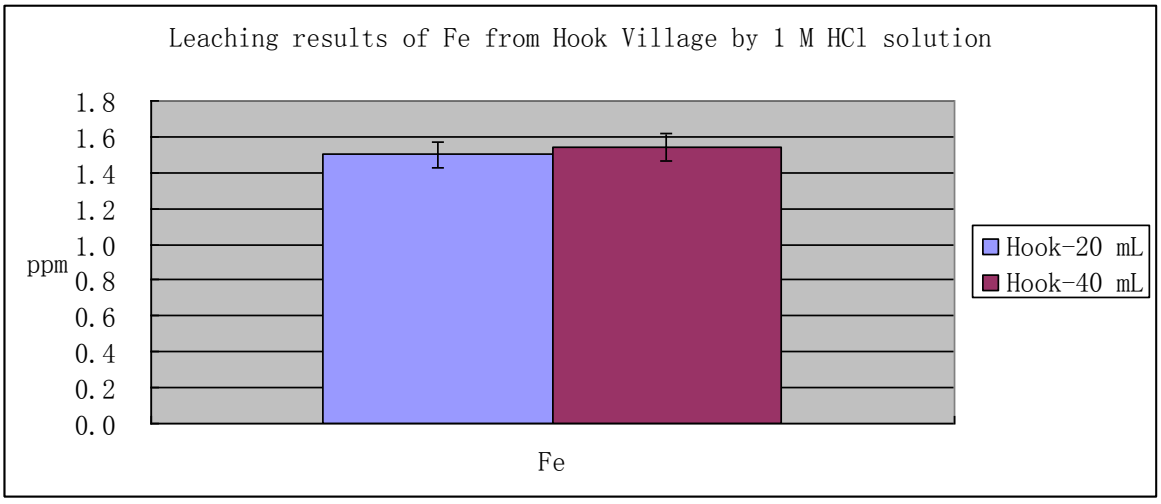
In Figure 4.6.2.2 and Figure 4.6.2.3 are compared the spiking experiment when using the same matrix 0.5 M H_2SO_4 with the same percentage but different kinds of sulfate. Although $CaSO_4$ is slightly soluble in water (2.4 g / L at 25 °C) while Na_2SO_4 is soluble in water (19.2 g / 100 mL at 20 °C), both of the two sulfates led to less Pb^{2+} ions being extracted out. And from Figure 6.2.2.2, it is shown that for the soil samples from Hook Village, when Na_2SO_4 was added, less Pb^{2+} ions can be leached out than when $CaSO_4$ is added. But Figure 6.2.2.3 shows the leaching results of soil samples from Parys Mountain, $CaSO_4$ caused less Pb^{2+} ions to be leached out.

4.7 Using different amounts of hydrochloric acid (HCl) with the same concentration as matrices

To investigate whether 20 ml of 1 M HCl solution is enough to leach out all of the leachable metal ions, a comparison experiment has been done. The soil samples from Hook Village and Parys Mountain were taken then leaching was carried out using 20 ml 1 M HCl solution and 40 ml 1 M HCl to get a comparison.

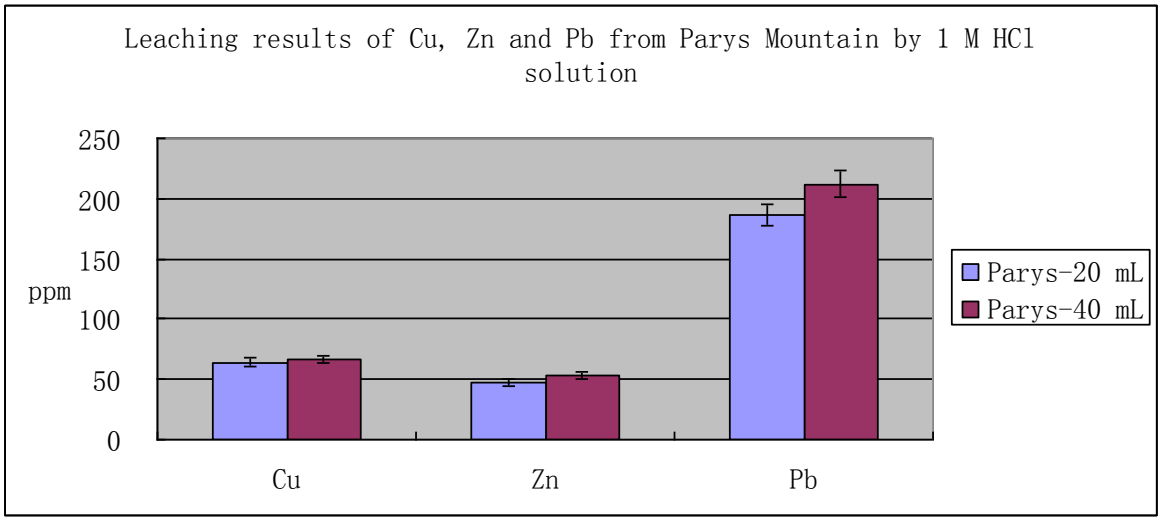


Figrue 4.7.1 Comparison of experiments to determine the concentration of Cu, Pb and Zn leached by 1 M HCl while using different amount of HCl (20 ml and 40 ml) from Hook Village and detected by AAS

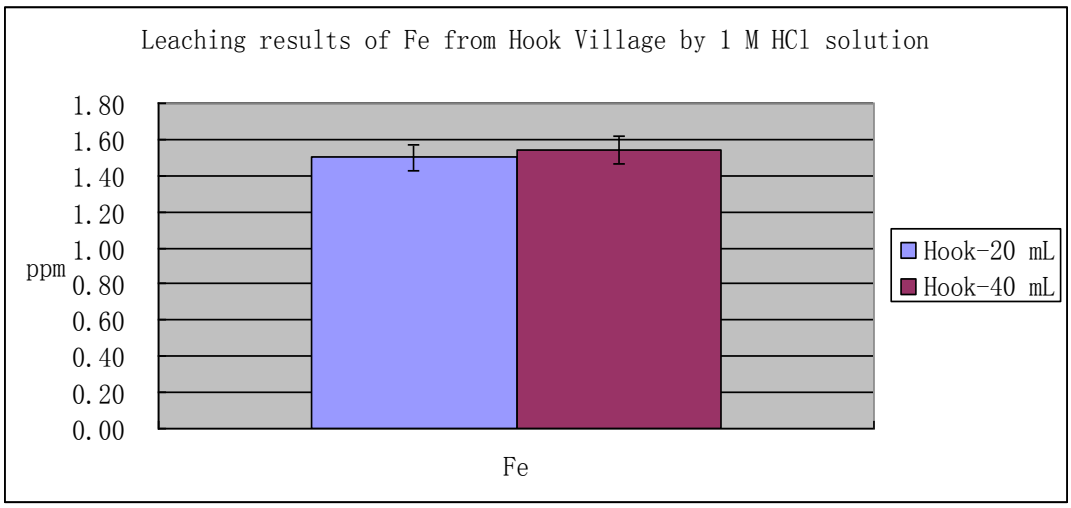


Figrue 4.7.2 Comparison of experiments to determine the concentration of Fe leached by 1 M HCl while using different amount of HCl (20 ml and 40 ml) from Hook Village and detected by AAS

From Figure 4.7.1 and Figure 4.7.2, it is easy to see that when using a greater volume of HCl solution (40 ml), the leaching results of Cu, Zn and Fe only differ slightly. It means that for the three selected metals, when the concentration of hydrochloric acid is 1 M, 20 ml solution is enough to remove all of the leachable metal ions and even on adding double the amount of acid solution with the same concentration there is no further leaching of metal ions from the solution. As the total amount of Fe in the soil is very high (4.69 % by XRF and 3.01 % by aqua regia), it also confirms that for this particular concentration of acid (1M) no further Fe^{2+} ions can be leached by increasing the volume of acid used. For lead, when using 40 mL HCl solution, the leaching results are a bit higher than when using 20 mL but the amount of Pb leached from the soil is not doubled. This result does, however, indicate that there are more extractable lead ions in the samples and 20 mL of 1 M HCl is perhaps not enough to leach out all of them.



Figrue 4.7.3 Comparison of experiments to determine the concentration of Cu, Pb and Zn leached by 1 M HCl while using different amount of HCl (20 ml and 40 ml) from Parys Mountain and detected by AAS



Figrue 4.7.4 Comparison of experiments to determine the concentration of Fe leached by 1 M HCl while using different amount of HCl (20 ml and 40 ml) from Parys Mountain and detected by AAS

Figure 4.7.2.3 and Figure 4.7.4 are quite similar to Figure 4.7.1 and Figure 4.7.2. It is easy to see that for the soil samples from Hook Village and Parys Mountain, more acid solution added into the soil samples does not leach out more metal ions.

4.8 Discussion and conclusion

In this chapter, four different acids (aqua regia, hydrochloric acid, sulfuric acid and nitric acid) and different concentrations of these acids have been used to carry out leaching experiments for the soil samples from Hook Village and Parys Mountain.

Firstly, comparing the leaching results from the acids and the total concentrations of metals within the soil samples detected by XRF (see the figures below Figure 4.8.1- Figure 4.8.4),

it is shown that not all of the heavy metals from the soil samples can be leached out. Although Aqua regia is a very strong acid and can extract a higher proportion of the metals than the other three acids, only 64.17% of Fe, 80.31 % of Cu, 45.57 % of Zn and 74.86 % of Pb from Hook village soil samples have been extracted out. And For Parys Mountain, 70.70 % of Fe, 95.33 % of Cu, 91.55 % of Zn and 83.46 % of Pb have been extracted out.

Secondly, soil leaching with HCl solution, H_2SO_4 solution and HNO_3 solution successfully removed Pb, Zn, Cu and Fe from soil samples from both Hook Village and Parys Mountain. HCl, H_2SO_4 and HNO_3 solution are good matrices for leaching experiments, but when the acids have similar concentrations they may have different efficacies of soil leaching. Sulfuric acid is generally a poorer leachate than hydrochloric acid. And for certain heavy metal such as lead, HCl can leach out more than double the quantity of metal ions than H_2SO_4.

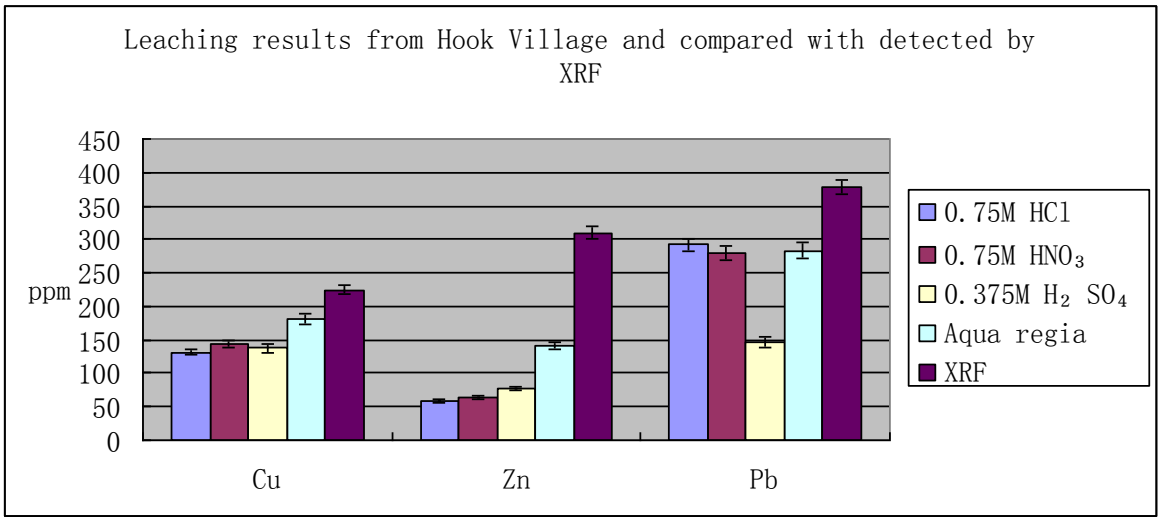


Figure 4.8.1 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and Aqua regia as matrices and detected by AAS and soil samples detected by XRF

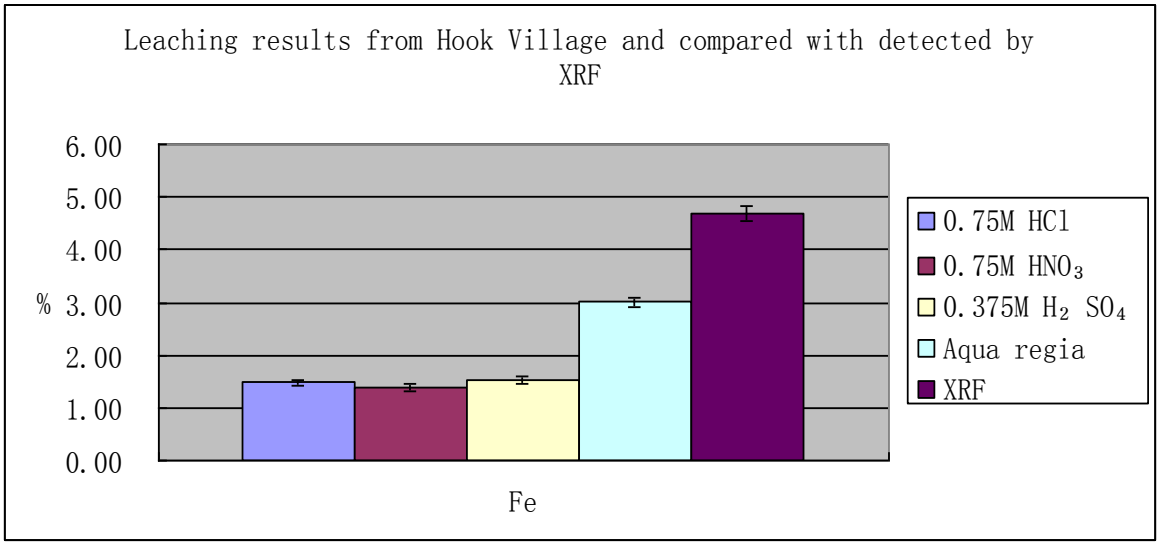


Figure 4.8.2 A graph showing the percentage of Fe leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and Aqua regia as matrices and detected by AAS and soil samples detected by XRF

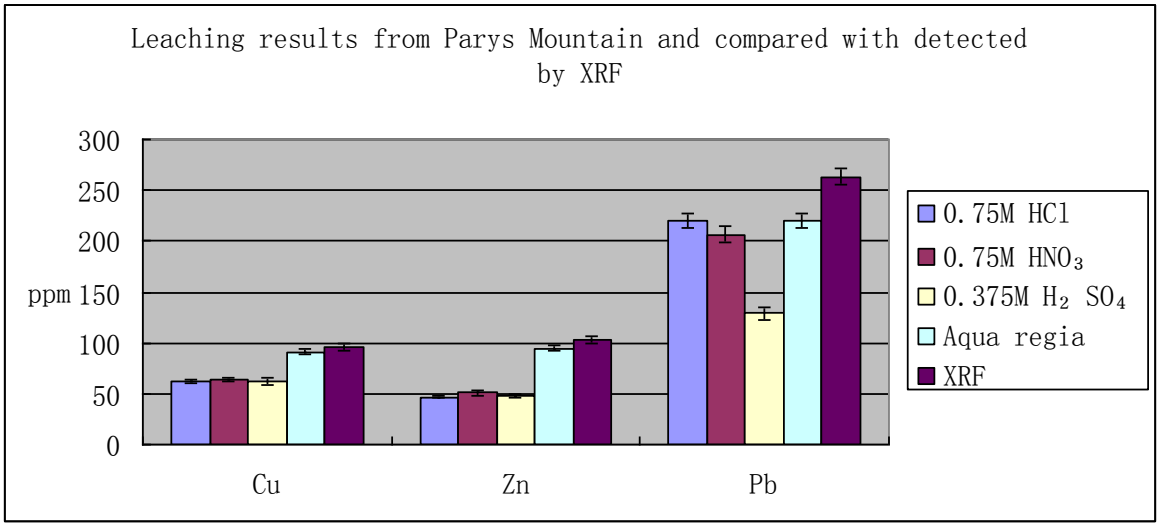


Figure 4.8.3 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and Aqua regia as matrices and detected by AAS and soil samples detected by XRF

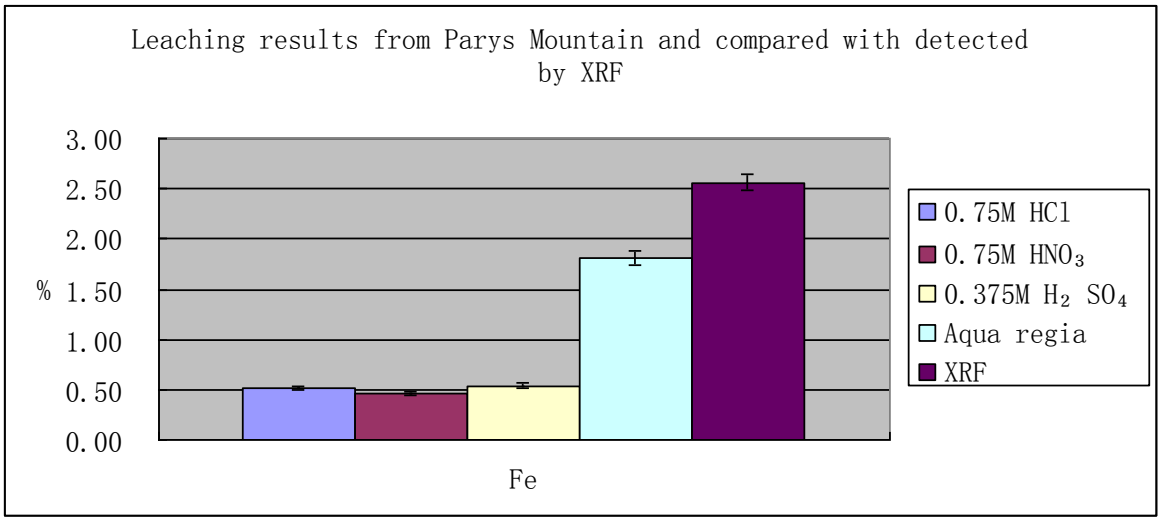


Figure 4.8.4 A graph showing the percentage of Fe leached from Parys Mountain using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4 and Aqua regia as matrices and detected by AAS and soil samples detected by XRF

It is also shown that the amount of metal leached from one of the soil samples does not always increase as the acidity increases. For the soil samples from both Hook Village and Parys Mountain, when using HCl solution and for copper and lead, when the concentration of hydrochloric acid is more than 0.75 M, there is no further leaching of metal ions from the solution. When using H_2SO_4 solution, the increase of H_2SO_4 solution concentration just induces more copper, zinc and iron ions to be leached out while Pb gives a different result. The lead leaching results gave a curve with no clear trend when using increasing concentrations of H_2SO_4 solution. And when using HNO_3 solution, for the soil samples from Hook Village, the increase of HNO_3 solution concentration induces more copper and zinc ions to be leached out. But for Pb, while the amount of leached metal increases rapidly from 0.25 M HNO_3 to 0.5 M HNO_3 (263ppm to 287 ppm) at concentrations above 0.5 M HNO_3 the amount of lead leached out does not increase so much. For the soil samples from Parys Mountain, the increase of HNO_3 solution concentration induces more copper and lead ions to be leached out. But for zinc, the leaching results from six different concentrations of nitric acid are similar. This result may suggest that the 0.25 M HNO_3 has already leached out all the leachable zinc ions. And from Figure 4.8.1, it is easy to find that

the amount of zinc extracted from the Hook Village samples is very low, even with aqua regia. Under these conditions less than the half of the total zinc is leached out. One hypothesis is that it is possible that zinc in these soil samples is present in a form where it is not readily leached e.g. trapped within or chemically bonded to a silicate mineral.

Because of the low solubility of lead sulfate, the higher concentrations of sulfuric acid do not necessarily lead to the extraction of more lead. The soil samples from Hook Village leached most when using 0.05 M H_2SO_4 solution as matrix. But for the samples from Parys Mountain, 0.5 M H_2SO_4 solution can leach the most lead ions from the solution. One reason may be that the two sites have different acidity. Another reason may be that the lead ions in the two sites have different chemical content such as galena (PbS), anglesite ($PbSO_4$), minium (Pb_3O_4) and cerussite ($PbCO_3$). Unfortunately, it has not proved to be possible to determine exactly what lead mineral are present in these samples. The leaching results of Pb using different concentrations of H_2SO_4 show a curve with no clear trend. It may because $PbSO_4$ is very slightly soluble in water, slightly soluble in dilute sulfuric acid, more soluble in concentrated sulfuric acid [23], so that when the concentration of sulfuric acid is increasing, the H^+ ion concentration is also increased which may enhance the solubility of lead compound. But at the same time, the amount of SO_4^{2-} also increases, and these ions may lead to more $PbSO_4$ precipitation. It may therefore reduce the solubility of lead ions. In other words the overall solubility of $PbSO_4$ in H_2SO_4 depends upon a number of related equilibrium reactions and is not straightforward to predict. The spiking experiments trend to confirm this hypothesis. When different amounts of $CaSO_4$ and Na_2SO_4 were added into the soil samples, the more the sulfate added, the less Pb ions can be leached out.

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Chapter 5 Chelating Ligands in Leaching Experiments

5.1 Introduction

Heavy metals in soil are an important issue due to the adverse effects they may have on human health and the environment [1, 2]. Chapter 4 described studies of the acidification process for the recovery of heavy metals from soil samples. In that chapter, different acids and different concentrations of acids were used as matrices. Chelating agents also play an important role in the leaching process. Chelating agents can combine heavy metals from the soil solid phase and form water-soluble metal-chelant complexes, which can be leached out of the soil [3, 4].

In this project, ethylenediaminetetraacetic acid (EDTA) was used as a model for chelating agents. EDTA is a colourless, slightly water-soluble solid. It has been shown to be one of the most popular and effective chelating agents for leaching heavy metals [3, 5]. Lombi *et al.* found that most of the heavy metals in soil can combine with EDTA [6]. EDTA can combine with a proportion of heavy metal ions to form stable complexes [7] and the most common coordination ratio is 1:1. It can react with nearly all metal ions and nearly all of the coordination compounds so formed have good solubility and good stability.

Although EDTA is a good matrix for leaching experiments, the mode of EDTA addition is an important factor in controlling the behaviour of metal leaching. In 2001, Sun used EDTA to leach heavy metals from contaminated soil. In that study, the soil was extracted using batch and column experiments [8]. In a batch experiment, EDTA extracted four heavy metals (Pb, Zn, Cu and Cd) in similar quantities. But in column leaching with EDTA, the mobility of the four metals was different. Copper was the most mobile of the four heavy metals while lead was the least mobile. The mobility of zinc and cadmium was slightly lower than that of copper. The results suggest that the lability of metals in soil, the kinetics

of metal desorption /dissolution and the mode of EDTA addition were the main factors controlling the behaviour of metal leaching with EDTA [8].

When using EDTA as matrix, even a small change of pH value can cause different results. The relationship between EDTA (H_4Y) distribution coefficient and pH value of the solutions is as follows:

The equilibrium constants are as follows: [9]

$H_6Y^{2+} \leftrightharpoons H^+ + H_5Y^+$ $K^{\theta}_{a1}=c(H^+)\cdot c(H_5Y^+)/\ c(H_6Y^{2+})=10^{-0.9}$

$H_5Y^+ \leftrightharpoons H^+ + H_4Y$ $K^{\theta}_{a2}=c(H^+)\cdot c(H_4Y)/\ c(H_5Y^+)=10^{-1.6}$

$H_4Y \leftrightharpoons H^+ + H_3Y^-$ $K^{\theta}_{a3}=c(H^+)\cdot c(H_3Y^-)/\ c(H_4Y)=10^{-2.0}$

$H_3Y^- \leftrightharpoons H^+ + H_2Y^{2-}$ $K^{\theta}_{a4}=c(H^+)\cdot c(H_2Y^{2-})/\ c(H_3Y^-)=10^{-2.67}$

$H_2Y^{2-} \leftrightharpoons H^+ + HY^{3-}$ $K^{\theta}_{a5}=c(H^+)\cdot c(HY^{3-})/\ c(H_2Y^{2-})=10^{-6.16}$

$HY^{3-} \leftrightharpoons H^+ + Y^{4-}$ $K^{\theta}_{a6}=c(H^+)\cdot c(Y^{4-})/\ c(HY^{3-})=10^{-10.26}$

Thus a graph may be plotted of the concentrations of individual ions against pH. This graph is shown in Figure 5.1.1.

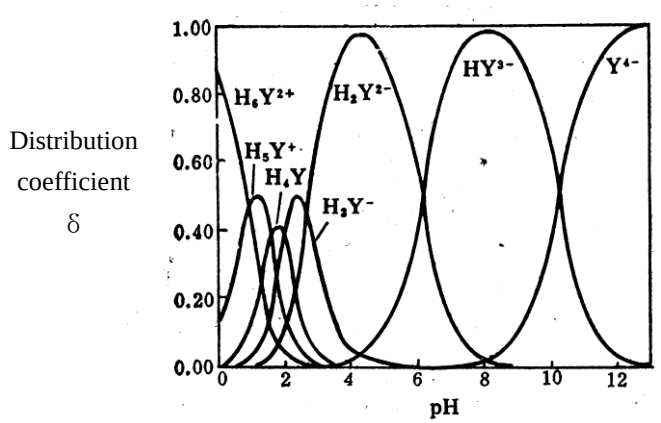

Figure 5.1.1 The relationship between the EDTA (H_4Y) distribution coefficient and the pH value of the solutions copied from reference [9]

As the solubility of fully protonated EDTA (H_4Y) is quite low, for the leaching experiments described in this chapter EDTA salts were used.

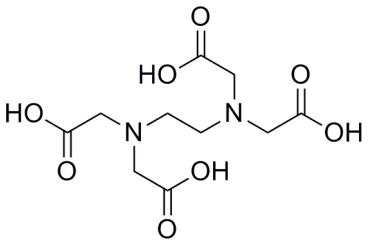

Figure 5.1.2 the structure of EDTA

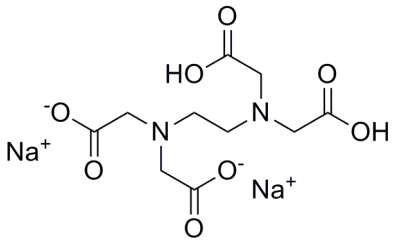

Figure 5.1.3 the structure of EDTA-2Na

Early EDTA studies [10, 11, 12] mostly focused on the efficacy when using EDTA solution as a matrix, but there is a question: whether different EDTA sodium salts may have the same effect on the amount of metal leached from a soil sample? In this chapter, EDTA-2Na and EDTA-4Na were selected as matrices for comparison.

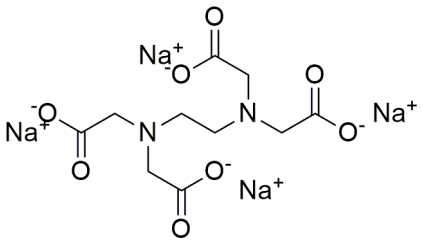

Figure 5.1.4 the structure of EDTA-4Na

As the chemical nature of EDTA is pH sensitive, the same EDTA salt but at different pH values was also selected for leaching experiments. Some "spike" experiments were also done to compare with the spike experiments described in chapter 4.

In this project, diethylenetriaminepentaacetic acid ($C_{14}H_{23}N_3O_{10}$), known as DTPA, was used as a comparison chelating agent. DTPA can remove metals such as Zn, Ni, Cu and Fe from both mineral and organic materials [13, 14]. In 1978, Lindsay *et al* found that DTPA can extract the plant-available metals in soil [15]. In 2003, Sahuquillo *et al* did research to confirm that DTPA is more suitable for calcareous soils while EDTA can leach out both carbonate-bound and organically-bound metals in soil [16]. And in 1999, Sharma *et al* used DTPA to determine the Cu, Zn, Pb and Mn concentrations from a benchmark soil of Indo-Gangetic plains [17]. They found DTPA-Zn has a positively correlated relationship with DTPA-extractable Fe, Cu and Mn.

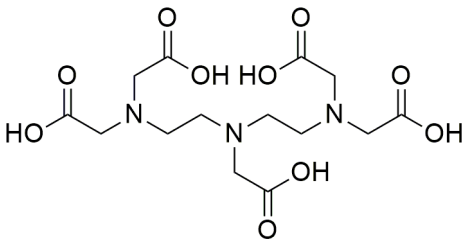

Figure 5.1.5 the structure of DTPA

5.2 Chelating ligands: EDTA-2Na, EDTA-4Na salts

When EDTA combines with divalent metallic ions (M^{2+}), the complex is formed in a ratio of 1:1. When the soil samples were leached by EDTA-2Na solution, the reaction with metal ions is written as:

$M^{2+} + H_2Y^{2-} \rightarrow MY^{2-} + 2H^{+}$ [18]

When the soil samples were leached by EDTA-4Na solution, the equilibrium is described as:

$M^{2+} + Y^{4-} \rightarrow MY^{2-}$ [18]

To investigate whether different EDTA sodium salts may have the same effect on the amount of metal leached from soil samples, leaching experiments have been carried out. Two different EDTA sodium salts have been selected in this experiment. 0.1 M EDTA-2Na solution and 0.1 M EDTA-4Na solution were used as matrices and compared as control groups.

The concentrations of Cu, Zn, Pb and Fe in extracts (leaching solutions, 0.1 M EDTA-2Na solution and 0.1 M EDTA-4Na solution) were determined by AAS (Nov AA 350 Analytik Jena) directly. The following graph shows the leaching results.

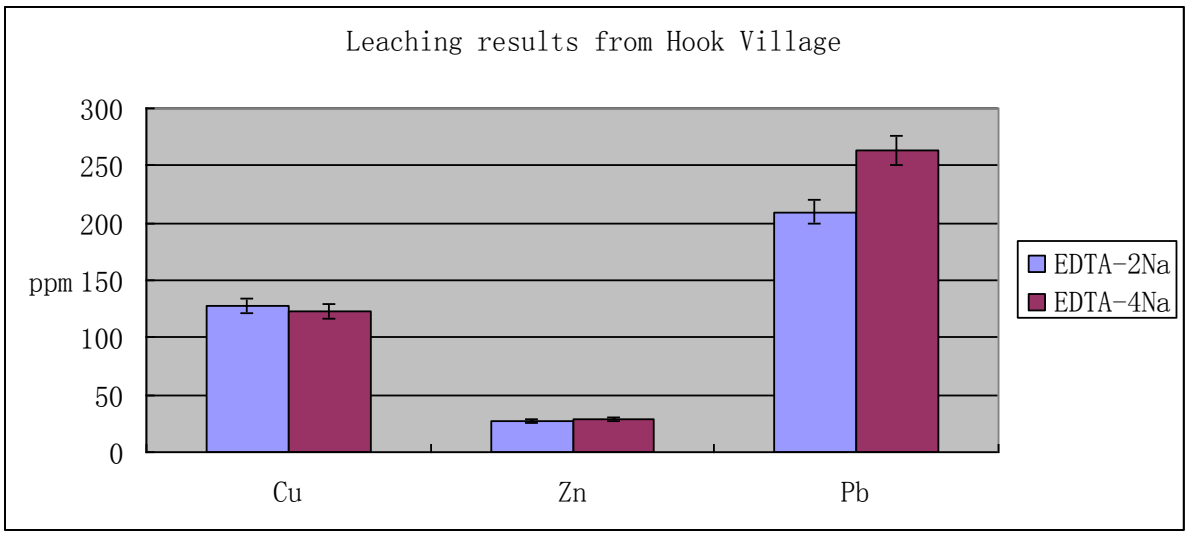

Figure 5.2.1 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.1M EDTA-2Na solution and 0.1 M EDTA-4Na solution and detected by AAS

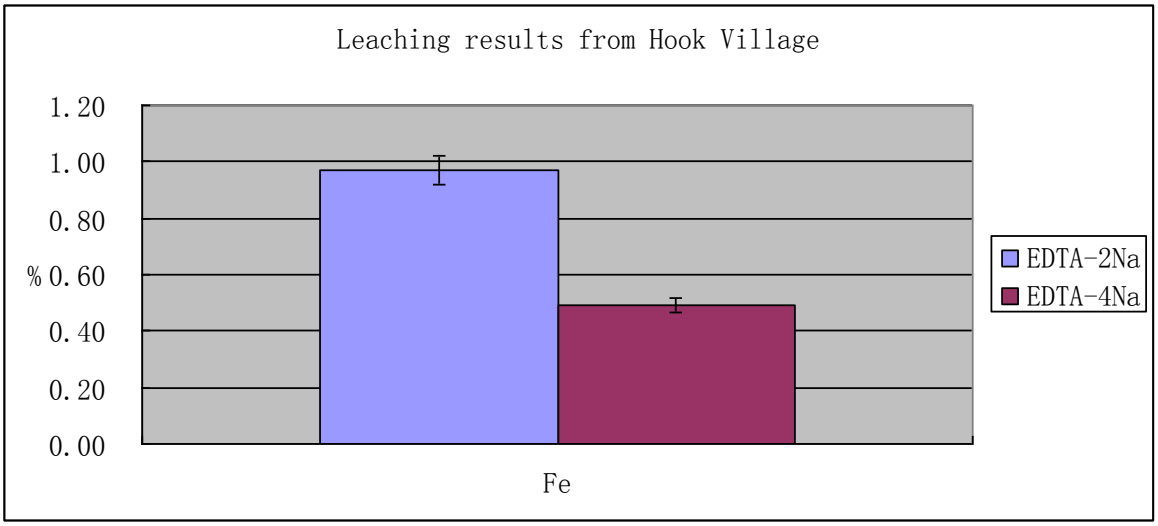

Figure 5.2.2 A graph showing the concentrations of Fe leached from Hook Village using 0.1M EDTA-2Na solution and 0.1 M EDTA-4Na solution and detected by AAS

Table 5.2.1 the concentrations of Cu, Zn, Pb and Fe leached from Hook village using 0.1 M EDTA-2Na and 0.1 M EDTA-4Na solution as matrices

	Cu (ppm)	Zn (ppm)	Pb (ppm)	Fe (%)
0.1 M EDTA-2Na	127	27	210	0.97
0.1 M EDTA-4Na	123	29	264	0.49

From data in Figure 5.2.1 and Figure 5.2.2, for copper and zinc, the two EDTA salt matrices have leached out similar amounts of the metals (for copper leached out by 0.1 M EDTA-2Na and 0.1 M EDTA-4Na the concentrations are 127 ppm and 123 ppm, respectively, and for zinc leached out by 0.1 M EDTA-2Na and 0.1 MEDTA-4Na they are 27 ppm and 29 ppm, respectively). Surprisingly, lead and iron leached with 0.1 M EDTA-2Na and 0.1 M EDTA-4Na showed an opposite effect. For iron ions, EDTA-2Na is more efficient than EDTA- 4Na solution while EDTA-4Na is better to leach out lead ions.

The pH value for 0.1 M EDTA-2Na solution is nearly 4 (this solution contains H_2Y^{2-}) while the pH value for 0.1 M EDTA-4Na solution is nearly 11 (this solution contains Y^{4-}). It means one of the salts is more acidic while the other one is more alkaline which may affect the leaching results. So one reason may be that for copper and zinc, the pH value does not affect the leaching results too much. But for iron, the acidic condition may help iron ions combine more with EDTA salts while for lead the alkaline condition makes it more favourable to combine lead ions with EDTA salts.

Another hypothesis is that metal size also has some relationship with leaching results and pH condition. The atomic weight for iron, copper, zinc and lead are 55.8, 63.5, 65.4 and 207.2 g / mol, respectively [19]. And the atomic radius for iron, copper, zinc and lead are 1.24 Å, 1.28 Å, 1.34 Å and 1.75 Å, respectively [19]. For lead, both atomic radius and atomic weight are bigger than those for iron which may induce lead ions to be leached

more effectively in 0.1 M EDTA-4Na solution.

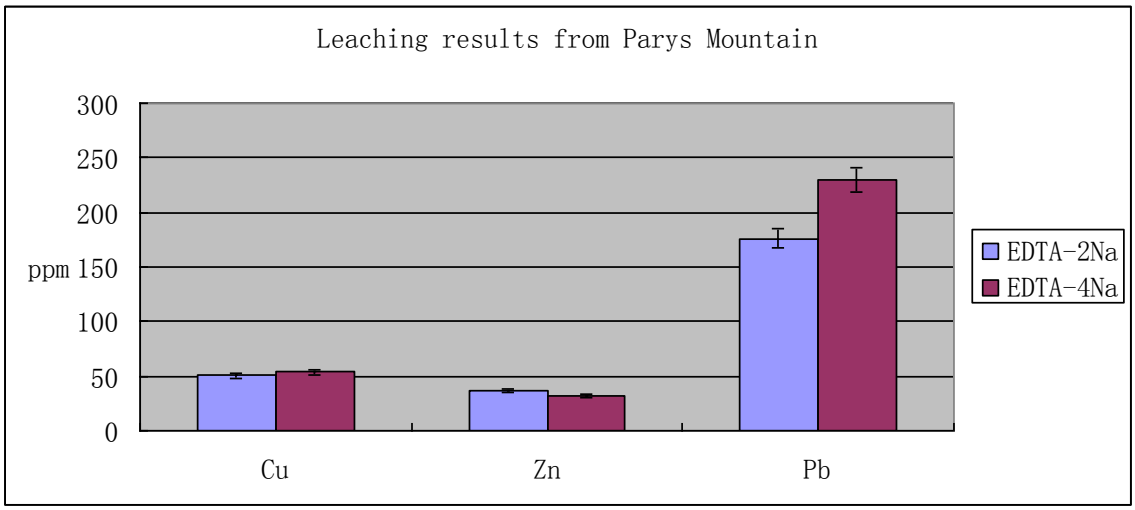

Figure 5.2.3 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.1M EDTA-2Na solution and 0.1 M EDTA-4Na solution and detected by AAS

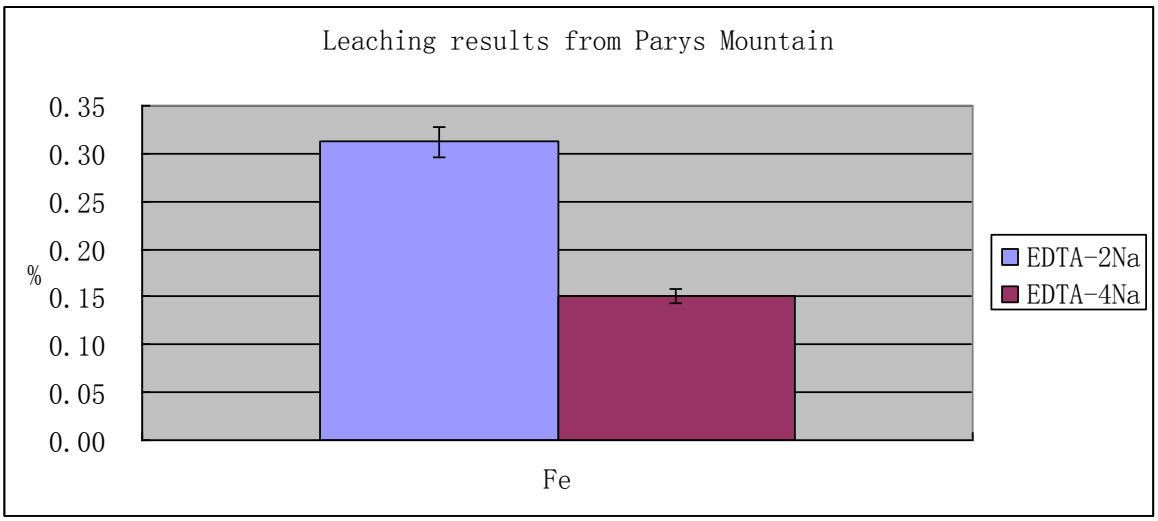

Figure 5.2.4 A graph showing the concentrations of Fe leached from Parys mountain using 0.1M EDTA-2Na solution and 0.1 M EDTA-4Na solution and detected by AAS

Table 5.2.2 the concentrations of Cu, Zn, Pb and Fe leached from Parys Mountain using 0.1 M EDTA-2Na and 0.1 M EDTA-4Na solution as matrices

	Cu (ppm)	Zn (ppm)	Pb (ppm)	Fe (%)
0.1 M EDTA-2Na	50	36	176	0.31
0.1 M EDTA-4Na	54	32	229	0.15

From the Figure 5.2.3 and Figure 5.2.4 above, the leaching results from Parys Mountain shows great similarity to those from Hook Village. For copper and zinc, the amount of metal leached out by 0.1 M EDTA-2Na and 0.1 M EDTA-4Na is quite similar (for copper, 50 ppm and 54 ppm, respectively, for zinc, 36 ppm and 32 ppm, respectively). For iron ions, EDTA-2Na solution is more efficient which the percentage of iron ions leached out is more than one time than iron ions leaching by 0.1 M EDTA-4Na. But for lead, 0.1 M EDTA-4Na is better to leach lead ions. This demonstrates that this trend is reproducible and is seen for soil samples from both sites investigated. The reason may be that for lead the alkaline conditions make combination of lead ions with EDTA salts more favourable. As such the following experiments were carried out to investigate whether the pH value of the EDTA sodium salt affects the leaching results.

5.3 EDTA salts with different pH value

In this experiment, 0.1 M EDTA-4Na was used as the matrix. Sodium hydroxide (2 M NaOH) solution and acetic acid (conc. HAc) were added into EDTA-4Na solution to change the pH value.

The original pH value for 0.1 M EDTA-4Na solution is 11.07 (Jenway 3020 pH meter, room temperature). To the first group of samples (sample 601- 608) sodium hydroxide was added to adjust the pH value to 12.45. To the second group of samples (sample 609-616) acetic acid was added to adjust the pH value to 4.65.

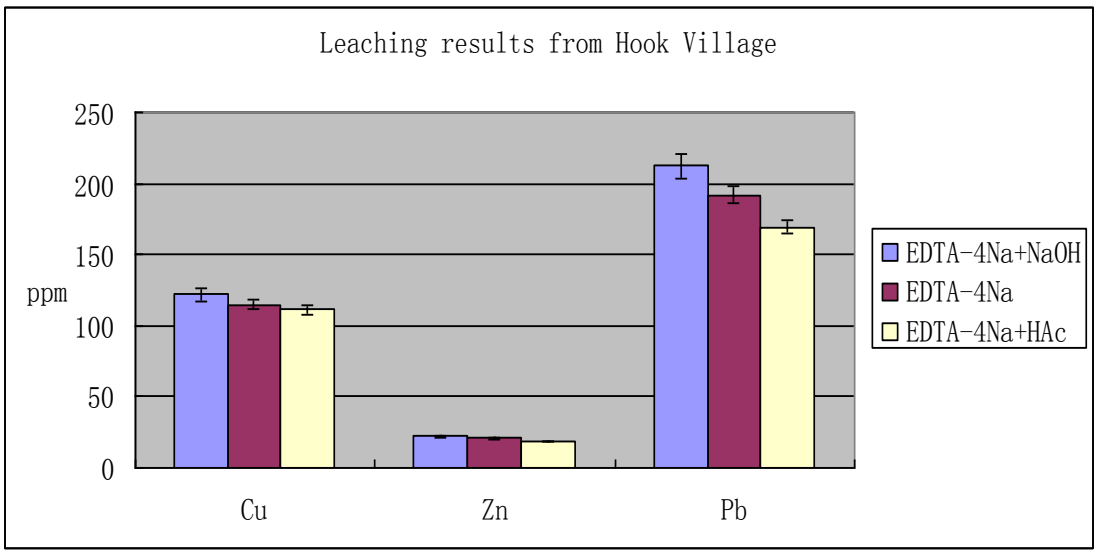

Figure 5.3.1 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.1M EDTA-4Na solution Groups and detected by AAS

From the Figure 5.3.1 above, it is easy to see that in the soil samples from Hook Village, for copper and zinc, even a pH value change from 12.45 to 4.65, does not affect the efficiency of the leaching process much. But for lead, the more alkaline the matrices, the less lead ions have been leached out. This result is similar to the step 5.2 that EDTA-4Na (pH value 11) leached out more lead ions than EDTA-2Na (pH value 4). And it can confirm the hypothesis that under alkaline conditions it is easier to combine lead ions with EDTA salts.

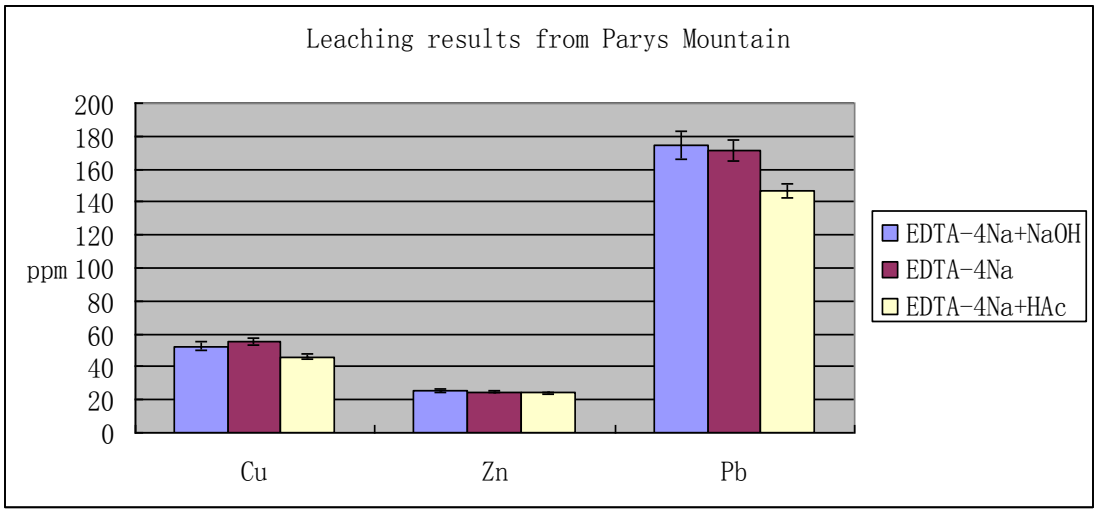

Figure 5.3.2 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.1M EDTA-4Na solution Groups and detected by AAS

From the Figure 5.3.2 above, the leaching results of the soil samples from Parys Mountain are quite similar to those from Hook Village. For copper and zinc, even the pH value change from 12.45 to 4.65 does not affect the leaching results very much. But for lead it may be seen that more lead ions are leached under more alkaline conditions. It is not entirely clear why this should be the case but it probably demonstrated that Pb^{2+} ions interact more readily with the Y^{4-} ions which exist at higher concentration at the higher pH. This may, in turn, reflect the larger size of the Pb^{2+} cation when compared with the other cations studied. The results show that the precise pH conditions are important and that different metals may be leached more efficiently from soils at different pH values.

5.4 Spiking experiments

In chapter 4, it is shown that when different amounts of $CaSO_4$ are added into soil samples

using H_2SO_4 as the matrix, the leaching results for lead will be quite different. The more $CaSO_4$ is added into the soil samples, the less Pb ions can be leached out. So in this chapter, different amounts of $CaSO_4$ (slightly soluble 2.4 g / L at 25 °C) and $CaCO_3$ **(**insoluble in water 15 mg / L at 25 °C**)** [19] were added into soil samples and using EDTA-2Na as matrix to find whether there is any difference.

5.4.1 Addition of different amounts of $CaSO_4$ to soil samples and leaching by EDTA-2Na

The soil samples from Hook Village and Parys Mountain were taken and to them were added different amounts of $CaSO_4$ and then leaching was carried out using 20 mL 0.1 M EDTA-2Na solution to get a comparison. To the samples from each site were added 8 % and 16 % of $CaSO_4$, respectively.

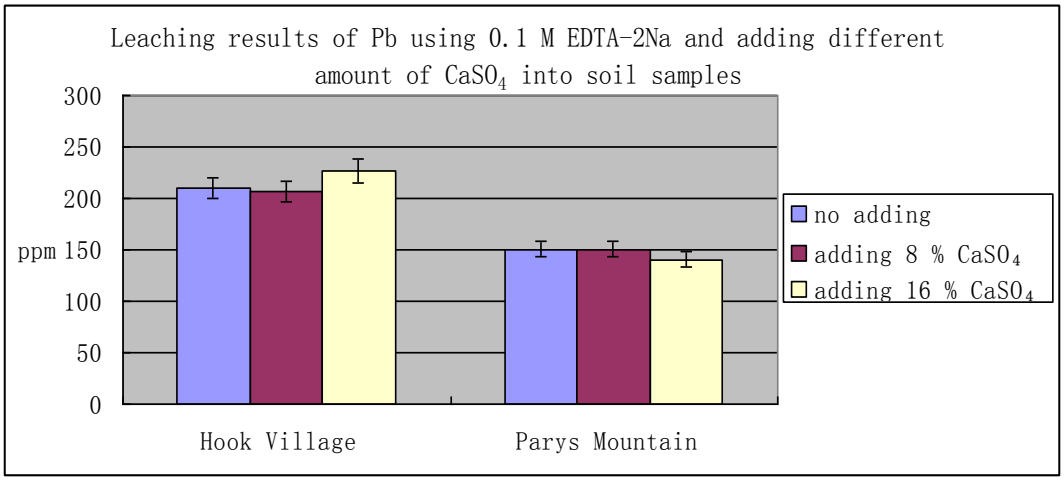

Figure 5.4.1 Comparison of spiking experiments to determine the concentration of Pb leached by 0.1 M EDTA-2Na solution while adding different amount of $CaSO_4$ (adding nothing, 8% $CaSO_4$ and 16 % $CaSO_4$) from Hook Village and Parys Mountain and detected by AAS

From the figure above, it is shown that for lead in soil samples from both sites, if different amounts of $CaSO_4$ were added it does not affect the leaching results very much. It suggests that lead ions first combine with EDTA and the structure of the EDTA-Pb complex is stable. EDTA combines efficiently with Pb^{2+} so the low solubility of $PbSO_4$ is not so important here as it is when considering leaching using acid matrices such as HCl and H_2SO_4.

5.4.2 Addition of different amounts of $CaCO_3$ to soil samples and leaching by EDTA-2Na

The content of calcium carbonate can affect the mobility of trace elements from soil samples [20, 21]. The $CaCO_3$ content of the soil samples has been detected by thermal analysis in chapter 3-3.2.1. Hook Village samples have 3.10 % ± 0.43 % calcium carbonate content while Parys Mountain samples have 1.45 % ± 0.38 % calcium carbonate content. It is also noted that lead carbonate is insoluble in water. In these experiments different amounts of calcium carbonate were added to the samples to investigate whether the leaching results will still be affected when using EDTA-2Na as the matrix.

The soil samples from Hook Village and Parys Mountain were taken and to them were added different amounts of $CaCO_3$ and then leaching was carried out using 20 mL 0.1 M EDTA-2Na solution to get a comparison. To the samples from each site were added 8 % and 16 % of $CaCO_3$, respectively.

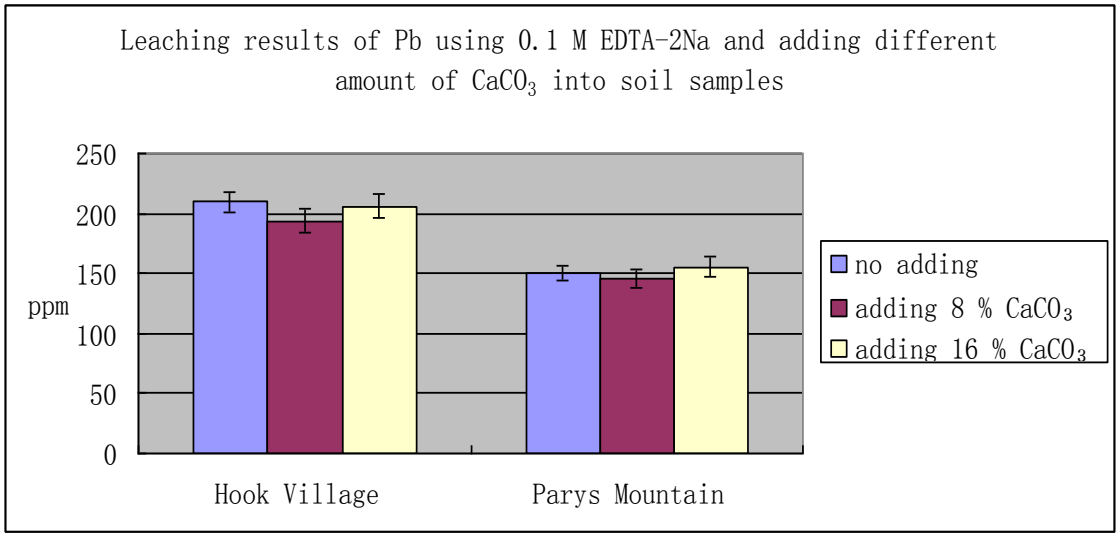

Figure 5.4.2 Comparison of spiking experiments to determine the concentration of Pb leached by 0.1 M EDTA-2Na solution while adding different amount of $CaCO_3$ (adding nothing, 8 % $CaCO_3$ and 16 % $CaCO_3$) from Hook Village and Parys Mountain and detected by AAS

From the figure above, when adding different amounts of $CaCO_3$ into soil samples, the leaching results for lead does not change too much. The leaching results when adding $CaCO_3$ are similar to those when adding different amounts of $CaSO_4$. The results suggest two important inferences. First it suggests that interference by calcium ions in the leaching experiments with EDTA is not very significant. Second, it confirms that EDTA forms a strong complex with Pb^{2+} which means that the insolubility of $PbSO_4$ and $PbCO_3$ is not so important. In other words EDTA can readily extract Pb^{2+} even in the presence of SO_4^{2-} and CO_3^{2-} .

5.5 The results of leaching experiments using the chelating ligand: DTPA

DTPA is another chelating ligand and the leaching results using this ligand have been compared with those using EDTA. The DTPA standard extraction matrix was made by mixing 0.005 M DTPA, 0.1 M triethanolamine (TEA) and 0.01 M $CaCl_2$ [15, 22, 23]. Then the pH value of the solution was adjusted to 7.34 by adding concentrated HCl.

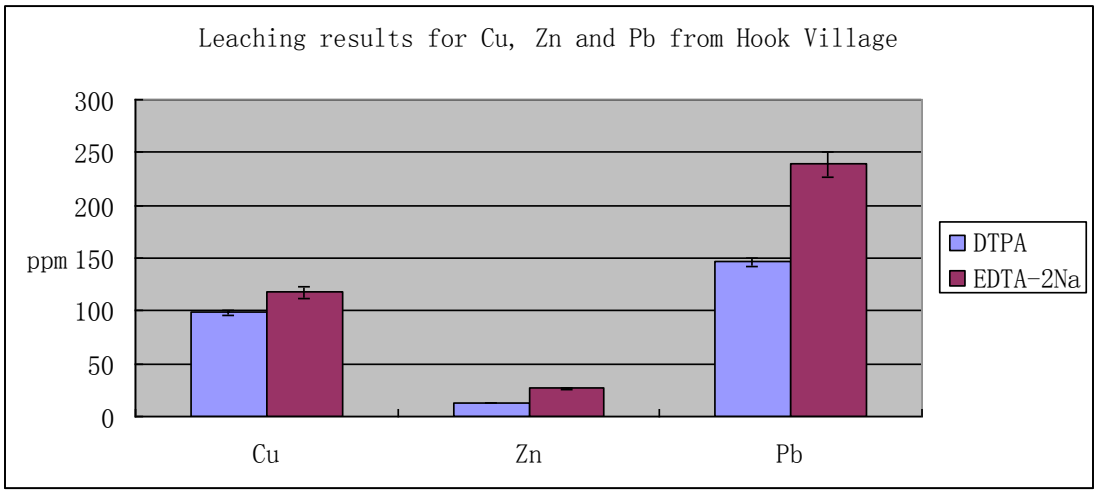

Figure 5.5.1 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.1 M EDTA-2Na and 0.005 M DTPA and detected by AAS

From the figure above, it shows that from the soil samples from Hook Village, both DTPA and EDTA can leach out the heavy metals. Here it must be noted that DTPA has a 20-times lower concentration (0.005 M) than does the EDTA matrix (0.1 M). Thus for Cu, Zn and Pb, DTPA is the much stronger leaching agent. Interestingly the total concentration of zinc detected by XRF from Hook Village is 309 ppm. DTPA only leached out 13 ppm zinc while EDTA leached out 26 ppm zinc. This suggests that neither EDTA nor DTPA are suitable matrices to leach out zinc from soil samples (at least under the conditions used in

this experiment).

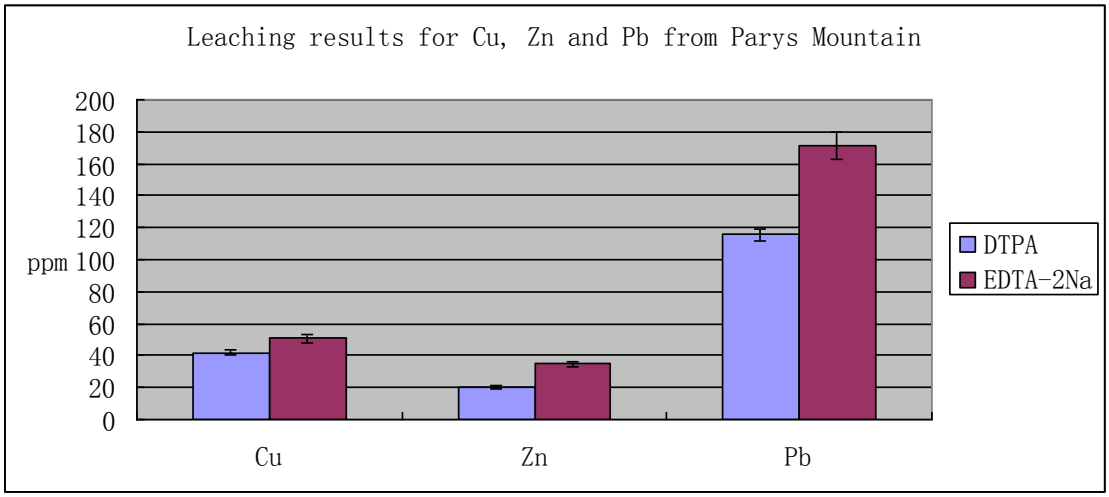

Figure 5.5.2 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.1 M EDTA-2Na and 0.005 M DTPA and detected by AAS

The leaching results for Parys Mountain samples are quite similar to those for the Hook Village samples. DTPA can extract Cu, Zn and Pb from the soil samples and with greater efficiency than EDTA. Once again only low concentrations of zinc are extracted.

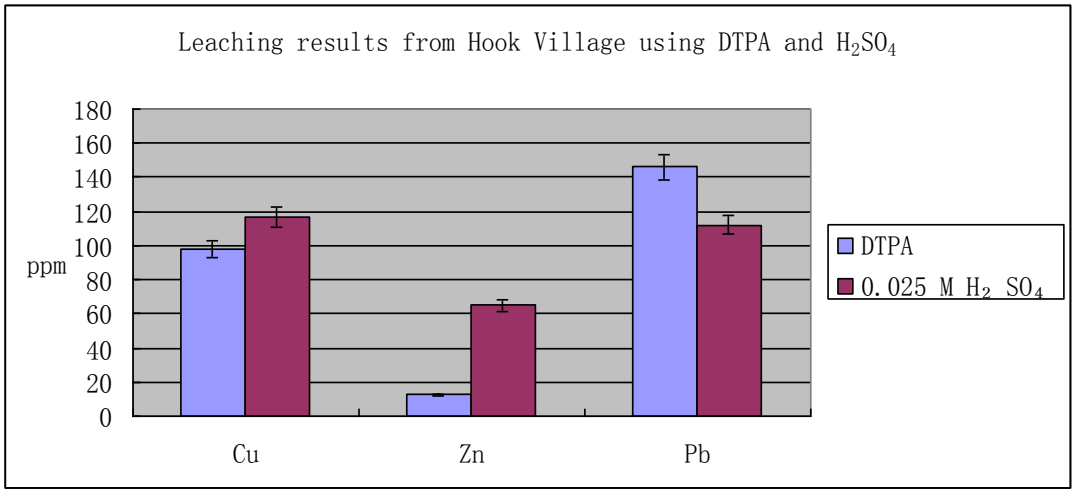

Figure 5.5.3 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.005 M DTPA and 0.025 M H_2SO_4 and detected by AAS

The Figure 5.5.3 above shows a comparison of the soil samples leached by 0.005 M DTPA and 0.025 M H_2SO_4. It is clear that Cu, Zn and Pb have different leaching results. The concentrations of H_2SO_4 and DTPA are different (DTPA is much more dilute) so a direct comparison of the concentrations of the leached metals is not particularly informative. However, once again the results emphasise that H_2SO_4 is a poor matrix for leaching Pb^{2+} because of the insolubility of $PbSO_4$.

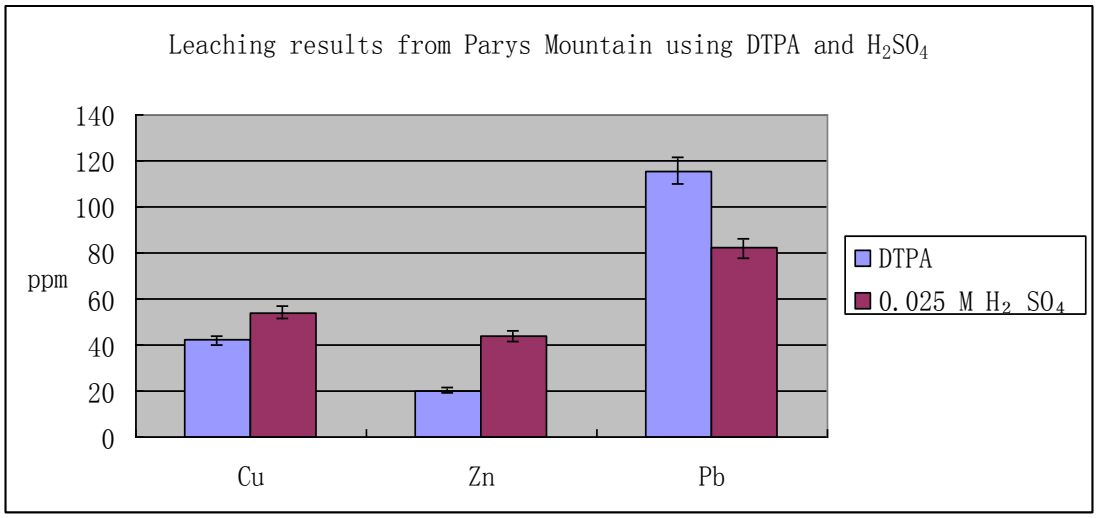

Figure 5.5.4 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.005 M DTPA and 0.025 M H_2SO_4 and detected by AAS

Figure 5.5.4 shows that the results for Parys Mountain samples back up those results for the Hook Village samples.

5.6 Discussion and Conclusion

In this chapter, different chelating agents (EDTA-2Na, EDTA-4Na and DTPA) have been used to carry out leaching experiments for the soil samples from Hook Village and Parys Mountain.

Firstly, the results show that different EDTA sodium salts all can extract heavy metals from soil samples. But different EDTA sodium salts may also affect the amount of metal leached out. For zinc and copper, the amount of metals leached out by the two EDTA salts is quite similar. For iron ions, EDTA-2Na can leach more than EDTA-4Na solution. But EDTA-4Na is better at leaching lead ions. One reason may be the different metal sizes where Pb^{2+} is the largest cation studied. The atomic radius for iron, copper, zinc and lead is 1.24 Å, 1.28 Å, 1.34 Å and 1.75 Å, respectively. Therefore further studies have been done to evaluate whether EDTA-4Na under different pH conditions will leach out different quantities of lead. Sodium hydroxide solution and acetic acid were added into EDTA-4Na solution to change the pH value and the leaching results confirm the hypothesis that under alkaline conditions it is easier to combine lead ions with EDTA salts. The results show that the precise pH conditions are important and that different metals may be leached more efficiently from soils at different pH values.

Secondly, some “spiking” experiments have been done to compare with the results when using inorganic acids as matrices. In chapter 4, when using H_2SO_4 as matrix, the more $CaSO_4$ is added into the soil samples, the less Pb ions can be leached out. So in this chapter,

different amounts of $CaSO_4$ (slightly soluble 2.4 g / L at 25 °C) and $CaCO_3$ **(**insoluble in water 15 mg / L at 25 °C**)** were added into soil samples when using EDTA-2Na as matrix to find whether there is any difference. The leaching results show that for lead, when different amounts of calcium salts were added into the soil samples it does not affect the leaching results very much. It suggests that EDTA combines more efficiently with Pb^{2+} than does SO_4^{2-}.

Finally, DTPA was used as a second chelating agent to carry out leaching experiments. Comparing the leaching results of EDTA and DTPA, it is shown that both DTPA and EDTA can leach out the heavy metals but DTPA is more efficient than EDTA. When comparing DTPA with diluted H_2SO_4 as leaching agents, for Pb, Zn and Cu it is found that DTPA is relatively more efficient at leaching Pb^{2+}. This is probably because of the insolubility of $PbSO_4$ which makes H_2SO_4 a poor leaching agent for Pb^{2+}.

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Chapter 6 The Role of Humic Acid in Leaching of Metals from Soils

6.1 Introduction

Humic substance is a heterogeneous mixture of naturally occurring organic substances [1, 2, 3] and it is widespread on the Earth's surface. It comes from the decay of the plants and animals in nature [2] and can be generally classified into three main fractions: humic acid, fulvic acid and humin. Humic acid is insoluble in water when the pH value is lower than 2 but is soluble at higher pH values. Fulvic acid is soluble in water under all pH conditions and humin is insoluble in water at any pH value [3, 4]. In this chapter, an essential extraction method has been developed at different pH requirement to separate the humic acid from soil samples.

Humic acid contains functional groups such as –COOH, –OH, and—NH_2 and these can affect the bonding distribution of cations of metals [3, 5, 6]. In 2006, Coles *et al.* carried out experiments to investigate the interactions of humic acid with lead and cadmium [7]. Lower pH values can help to remove the metals from solution by humic acid as at higher pH values, humic acid begins to dissolve. They obtained the conclusion that humic acid can act as an important material for metal removal. In 2006, Ghabbour *et al.* found that the metal mobility and bioavailability are affected by humic acid as the metal can be bound and released by solid humic acid in soils [8]. They obtained the results that Fe^{2+}, Pb^{2+} and Cu^{2+} can bind tightly to the solid humic acid from their soil samples and that Cu^{2+} binds more readily than Pb^{2+}. And In 2013, Kalina *et al.* did research to investigate the fractional extraction caused by interactions between humic acid and copper ions [9]. They also found that the humic acid has an effect on the mobility of metal ions in nature.

In the natural environment, fulvic acid and humic acid are found. In Chapter 5, EDTA was used as a model for polybasic acids present in the environment and some of the leaching results were affected by pH value. Here humic acid is investigated as a natural acid to find its effects on leaching experiments and whether the pH value of the leachates has some effect on the leaching results. In 1976, Stevenson showed that in general, the maximum amount of metal ion that can be bound to humic acid and fulvic acid is nearly equal to the content of the acidic functional groups [3]. Several factors can influence the quantity of metal bound by humic acid, including pH. In 2003, Martyniuk *et al.* conducted research about the reaction of metal ions with carboxylic groups (COOH) of the humic acid from brown coals and they reached the conclusion that the humic acid coordinates more strongly to metal ions at pH 6-7 than it does at pH 5 [10]. As the pH increases the COOH groups in the humic acid are deprontonated by the equation:

$$COOH \rightarrow COO^- + H^+.$$

The deprotonated COO^- groups will bind more strongly to the metal ions so humic acid should extract a higher proportion of metal ions at higher pH value. This is in line with the experiments of Martyniuk et al. who found that all of the carboxylate groups (COOH) in the humic acid engaged in binding to the metal ions at pH 6-7 while only a part of the total amount of the COOH groups did so at pH 5.

The pKa value for the dissociation of the carboxylic acid group is about 4 [11, 12, 13]. Thus the proportion of COO^- to COOH ions may be calculated from the Henderson- Hasselbalch equation [14, 15, 16]:

$$pH = Log_{10}([COO^-] / [COOH]) + pKa$$

Table 6.1 The proportion of COO^- to COOH ions at different pH values

pH	$[COO^-]$ / [COOH]
1	0.001
2	0.01
5	10
6	100
7	1000

In this research, to determine the effect of humic acid in leaching experiment, "spiking" experiments have been done. Different amounts of humic acid were added to the soil samples and these were leached with different matrices. As in the natural environment, soil may easily become more acidic in the presence, for example, of acid rain or run off from mining waste. And as acidification is a useful process for the recovery of heavy metals from contaminated soil [17], here leaching experiments have been carried out under acidic conditions. Deionised water and two different concentrations of HCl were selected as matrices. Then a comparison was made of the amount of metal leached from the soil by atomic absorption spectroscopy. It is expected that high humic acid concentrations may affect the leaching as the metal ion may bind to the humic acid. Where a complex is formed, high humic acid amounts should correspond to high metal ion concentrations in the same fraction. If a complex is not formed then the humic acid concentration probably will not be related to the metal concentration.

Besides atomic absorption spectroscopy, ultraviolet-visible spectroscopy was used [6, 18]. Experiments have been done in which the metal complexes were separated in a column [6,

[19]. By collecting the fractions, the humic acid can be measured using ultraviolet-visible spectroscopy and metals can be detected by atomic absorption spectroscopy. By comparing the results of UV-visible spectroscopy and atomic absorption spectroscopy for different individual fractions it should be possible to determine whether or not a complex has been formed between the humic acid and the metal ion. If a complex is formed then high metal ion concentrations should correspond to fractions where a high humic acid concentration is also indicated by a high absorbance in the UV-visible spectrum.

6.2 Extraction of humic acid from soil samples

In this section, a simple experiment has been done to confirm that there is humic acid in the soil samples from Hook Village and Parys Mountain.

Dry soil samples (5.5 g) were weighed and put into conical flasks (100 mL). Four samples from each site have been taken as replicates to get an average of the results. Sodium hydroxide solution (0.1 M NaOH, 40 mL) was added to the flask with the weighed soil sample and was labeled with the name of the site. The mixture was stirred for 2 hours (Fisher Scientific, Heating magnetic stirrer FB15001, room temperature) and then centrifuged to get the supernatant (MSE, Centaur 2, room temperature). Concentrated hydrochloric acid (HCl) was added to the supernatant and the pH value was adjusted between 1.0 - 2.0. The solution was centrifuged again this time get the residue which should be humic acid while the fulvic acid will remain in the solution. The residue was washed with deionised water to remove the nonhumic material. Then the residue was dried and weighed [2, 20, 21].

The experiments confirm that both the soil samples from Hook Village and Parys Mountain contain humic acid and the humic acid content in Hook Village samples is nearly 7.9 %

while the humic acid content in Parys Mountain is nearly 2.1 %. The results can be related to the background of the two sites. Hook Village was a coal mining area in the past which may lead to more humic acid in the soil samples.

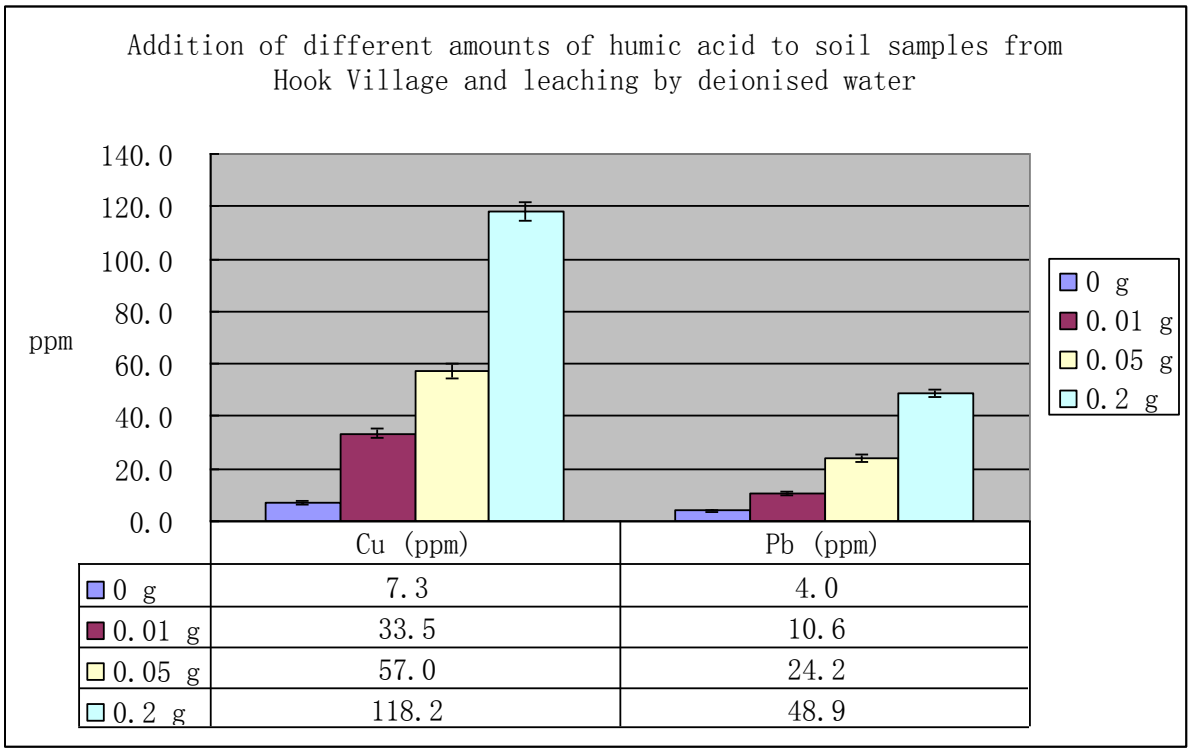
6.3 Humic acid spiking experiment

In chapter 4 and 5, spiking experiments were carried out where different amounts of $CaSO_4$ were added to soil samples using H_2SO_4 as the matrix. In this chapter, spiking experiments have been carried out to investigate the effects of humic acid.

Different amounts of humic acid (Sigma-Aldrich, CAS: 145-93-6) were added to the original soil samples (0.5 g). Leaching experiments were carried out with the spiked samples leached by deionised water, 0.05 M HCl and 1 M HCl respectively to check whether the additional humic acid affects the leaching results.

6.3.1 Addition of different amounts of humic acid with H_2O as the leachate

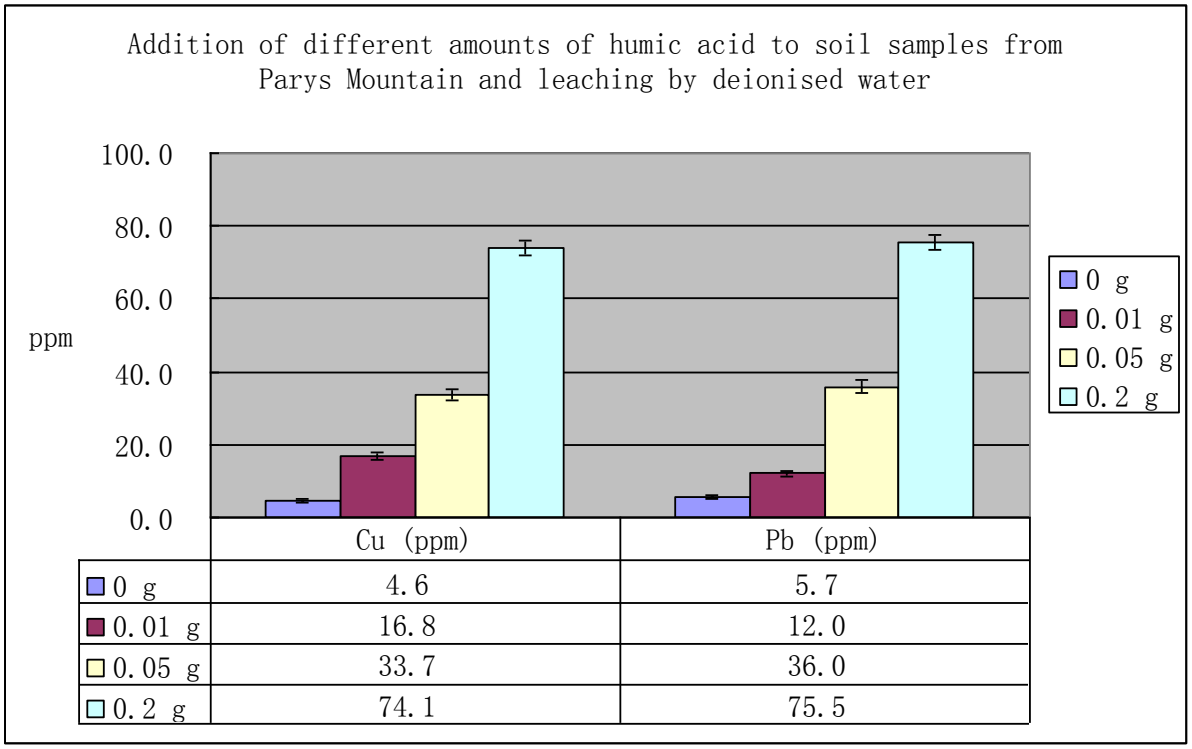
The soil samples from Hook Village and Parys Mountain were taken and to them were added different amounts of humic acid. Leaching experiments were carried out using 20 mL deionised water solution to get a comparison. To the samples from each site were added 0 g, 0.01 g, 0.05 g and 0.2 g of humic acid respectively.



	Cu (ppm)	Pb (ppm)
0 g	7.3	4.0
0.01 g	33.5	10.6
0.05 g	57.0	24.2
0.2 g	118.2	48.9

Figure 6.3.1.1 Comparison of spiking experiments to determine the concentration of Pb and Cu leached by deionised water while adding different amounts of humic acid (0 g , 0.01g, 0.05 g and 0.2 g) to the soil samples from Hook Village and detected by AAS

Deionised water is a very poor matrix. From Figure 6.3.1.1 above, it is shown that deionised water can only extract very little copper (7.3 ppm) and lead (4.0 ppm) from the soil samples from Hook Village. When 0.01 g humic acid was added to the soil samples, the leaching results for copper changed from 7.3 ppm to 33.5 ppm while the leaching results for lead changed from 4.0 ppm to 10.6 ppm. When adding more humic acid into the original samples i.e., 0.05 g humic acid the amount of copper and lead leached out of the samples was increased and when 0.2 g humic acid was added, the amount of metal leached out increased to 118.2 ppm for copper and 48.9 ppm for lead. It is easy to see that the increased amount of humic acid added to the soil samples leads to more Cu and Pb ions being leached out when using deionised water as matrix. It confirms that humic acid has a positive effect on leaching of metals when the matrix is deionised water.



	Cu (ppm)	Pb (ppm)
0 g	4.6	5.7
0.01 g	16.8	12.0
0.05 g	33.7	36.0
0.2 g	74.1	75.5

Figure 6.3.1.2 Comparison of spiking experiments to determine the concentration of Pb and Cu leached by deionised water while adding different amounts of humic acid (0 g, 0.01 g, 0.05 g and 0.2 g) to the soil samples from Parys Mountain and detected by AAS

From Figure 6.3.1.2, the leaching results from Parys Mountain are quite similar to those from Hook Village. When adding different amount of humic acid to the soil samples, the amounts of Cu and Pb leached from the soil samples keep increasing. And the more humic acid is added to the soil samples, more metal ions can be leached out by deionised water.

Comparing the spiking experiment results with the XRF results from chapter 3 section 3.2.4 (Table 6.3.1.1), it is easy to find that when adding humic acid to soil samples, different metals have different behaviour.

Table 6.3.1.1 Average concentration of Cu and Pb in soil samples from Hook Village and in Parys Mountain determined by XRF

	Cu	Pb
Hook Village	225.0 ppm	378.5 ppm
Payrs Mountain	95.8 ppm	263.5 ppm

Table 6.3.1.2 Percentages of Cu and Pb from soil samples leaching by deionised water while adding different amounts of humic acid and detected by AAS and compared with the results of original soil samples determined by XRF

Mass of humic acid / g	Cu-Hook	Pb-Hook	Cu-Parys	Pb-Parys
0 g	3.25 %	1.06 %	4.80 %	2.17 %
0.01 g	14.87 %	2.81 %	17.54 %	4.55 %
0.05 g	25.35 %	6.39 %	35.16 %	13.65 %
0.2 g	52.52 %	12.91 %	77.30 %	28.67 %

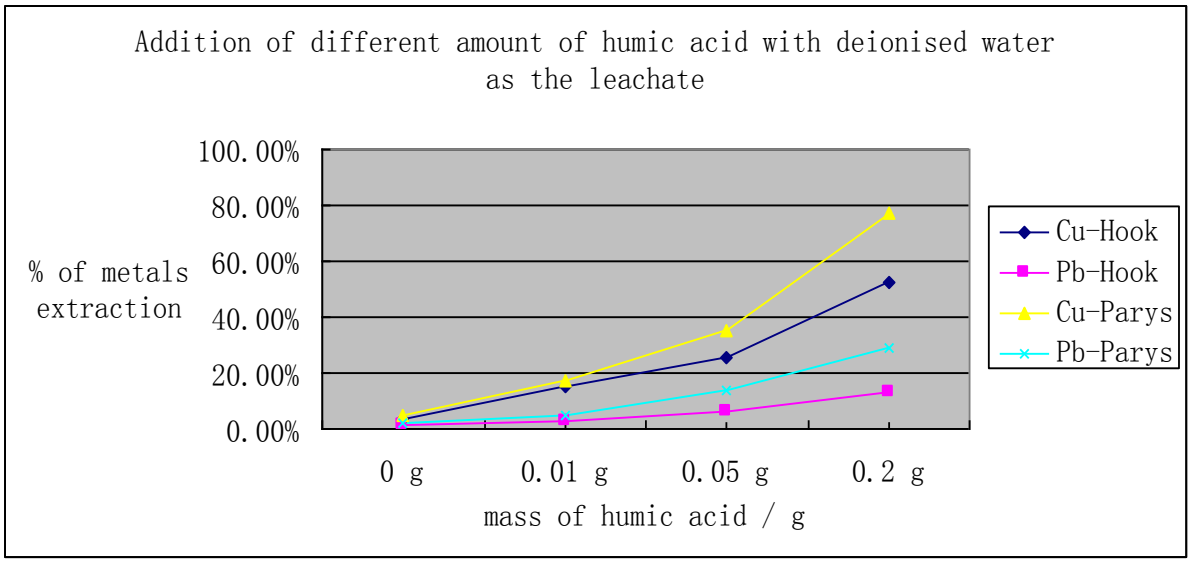


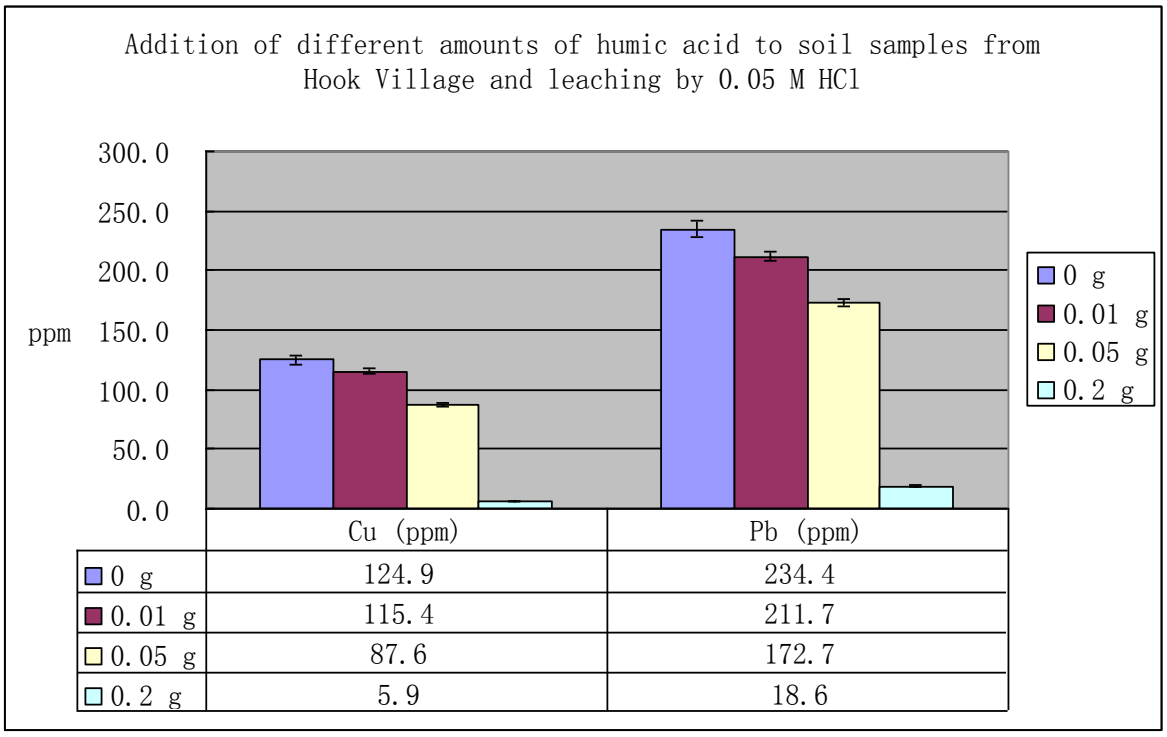
Figure 6.3.1.3 Percentages of Cu and Pb from soil samples leaching by deionised water while adding different amounts of humic acid and detected by AAS

Table 6.3.1.2 and Figure 6.3.1.3 show that from both sites, copper binds more strongly with humic acid when using deionised water as leachate. For Pb, when the mass of humic acid added to soil samples is increased, the percentages of Pb leached out increase from 1.06 % to 12.91 % in Hook Village and from 2.17 % to 28.67 % in Parys Mountain. But for Cu, the percentages show an even higher increase. When 0.2 g of humic acid added to soil samples from Hook Village, 52.52 % of copper ions can be leached out. And when 0.2 g of humic acid is added to soil samples from Parys Mountain, 77.30 % of copper ions are extracted. It is shown that humic acid can bind strongly with heavy metal ions and copper ions to form a complex with higher stability than the complex formed with lead. This conclusion supports findings obtained by P. Lubal *et al* in 1998 [5]. Their research investigated complexation properties of humic acids and they found that Cu^{2+} forms a complex with humic acid with the highest stability constant of a range of HA-metal ion complexes studied, namely those with Ba^{2+}, Pb^{2+}, Cd^{2+} and Ca^{2+}.

6.3.2 Addition of different amounts of humic acid salt with 0.05 M HCl as the leachate

When using deionised water as matrix, the humic acid has a positive effect on the amount of metal leached from the samples. In the second series of experiments dilute HCl was used as the matrix to compare with the results from section 6.3.1.

The soil samples from Hook Village and Parys Mountain were taken and to them were added different amounts of humic acid and then leaching was carried out using 20 mL 0.05 M HCl solution to get a comparison. To the samples from each site were added 0 g, 0.01 g, 0.05 g and 0.2 g of humic acid respectively.



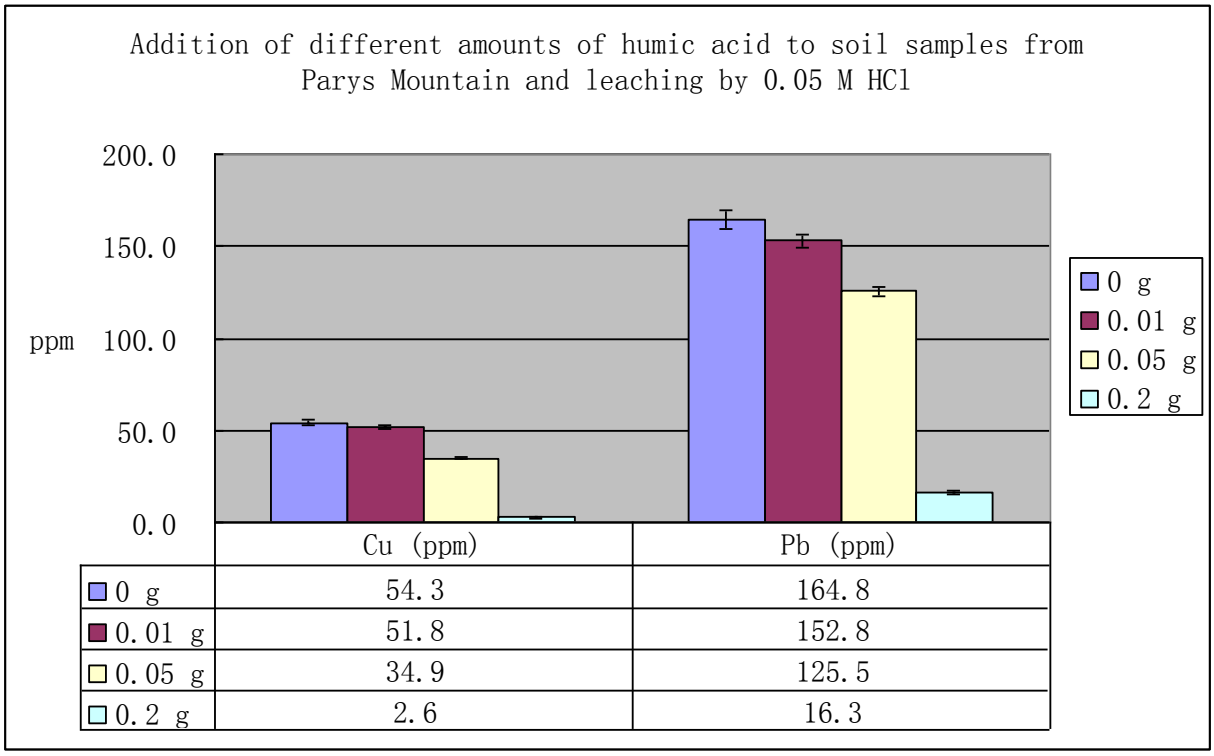
	Cu (ppm)	Pb (ppm)
0 g	124.9	234.4
0.01 g	115.4	211.7
0.05 g	87.6	172.7
0.2 g	5.9	18.6

Figure 6.3.2.1 Comparison of spiking experiments to determine the concentration of Pb and Cu leached by 0.05 M HCl solution while adding different amounts of humic acid (0 g, 0.01g, 0.05 g and 0.2 g) to the soil samples from Hook Village and detected by AAS

From Figure 6.3.2.1 above, it is easy to find the leaching results for 0.05 M HCl with different amounts of humic acid are quite different with those results from deionised water.

From Figure 6.3.2.1, it is shown that 0.05 M HCl with no humic acid added to the soil samples leaches more metals ions than do the other samples where humic acid is added. Nearly 124.9 ppm of copper and 234.4 ppm lead has been extracted from soil samples from Hook Village only by diluted HCl without additional humic acid. When 0.01 g humic acid is added to the soil samples, the leaching results for copper decreased from 124.9 ppm to 115.4 ppm while the leaching results for lead decreased from 234.4 ppm to 211.7 ppm. When more humic acid added into the samples, the amount of metal leached became much lower. Only 87.6 ppm of copper and 172.7 ppm of lead can be leached out when 0.05 g humic acid is added to the soil samples. When the total amount of humic acid increases to 0.2 g, only very little copper (5.9 ppm) and lead (18.6 ppm) can be extracted.

It is easy to see that for 0.05 M HCl, increased amounts of humic acid added to the soil samples leads to less Cu and Pb ions being leached out. In this section, humic acid has the opposite effect to its effect when water is the leachate.



	Cu (ppm)	Pb (ppm)
0 g	54.3	164.8
0.01 g	51.8	152.8
0.05 g	34.9	125.5
0.2 g	2.6	16.3

Figure 6.3.2.2 Comparison of spiking experiments to determine the concentration of Pb and Cu leached by 0.05 M HCl solution while adding different amounts of humic acid (0 g , 0.01g, 0.05 g and 0.2 g) to the soil samples from Parys Mountain and detected by AAS

From Figure 6.3.2.2, the leaching results from Parys Mountain are quite similar to those from Hook Village. The more humic acid is added to the soil samples, the less copper and lead ions can be leached out. It confirms that when using diluted acid as matrix, humic acid has an adverse effect upon the amount of metal leached from the sample.

Comparing the results using 0.05 M HCl with the XRF results from chapter 3 section 3.2.4 (Table 6.3.1.1), the percentages of Cu and Pb leached out are as follows:

Table 6.3.2 Percentages of Cu and Pb from soil samples leaching by 0.05 M HCl while adding different amounts of humic acid and detected by AAS and compared with the results of original soil samples determined by XRF

Mass of humic acid / g	Cu-Hook	Pb-Hook	Cu-Parys	Pb-Parys
0 g	55.52 %	61.92 %	56.65 %	62.53 %
0.01 g	51.28 %	55.93 %	54.09 %	57.99 %
0.05 g	38.93 %	45.63 %	36.42 %	47.65 %
0.2 g	2.63 %	4.93 %	2.67 %	6.19 %

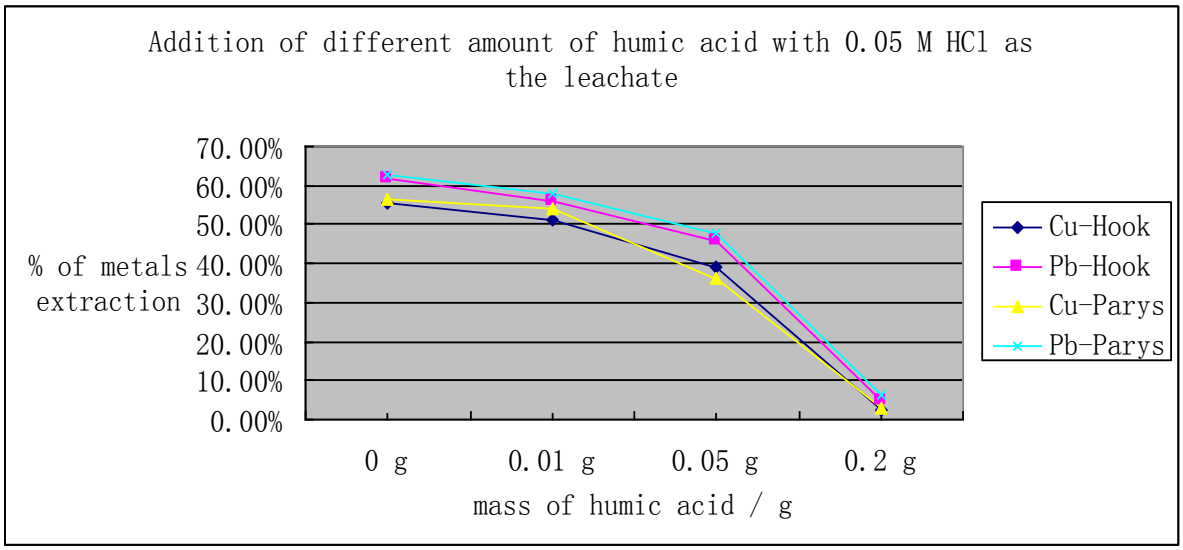


Figure 6.3.2.3 Percentages of Cu and Pb from soil samples leaching by 0.05 M HCl while adding different amounts of humic acid and detected by AAS

From Figure 6.3.2.3, it is easy to see that there is a notably decrease of leaching results for

both Cu and Pb when 0.2 g of humic acid is added to the soil samples. Only 2.63 % of Cu and 4.93 % of Pb from soil samples in Hook Village have been leached out and only 2.67 % of Cu and 6.19 % of Pb from soil samples in Parys Mountain have been extracted. The reason may be that humic acid reacts with diluted HCl first and acts as buffer solution as follows:

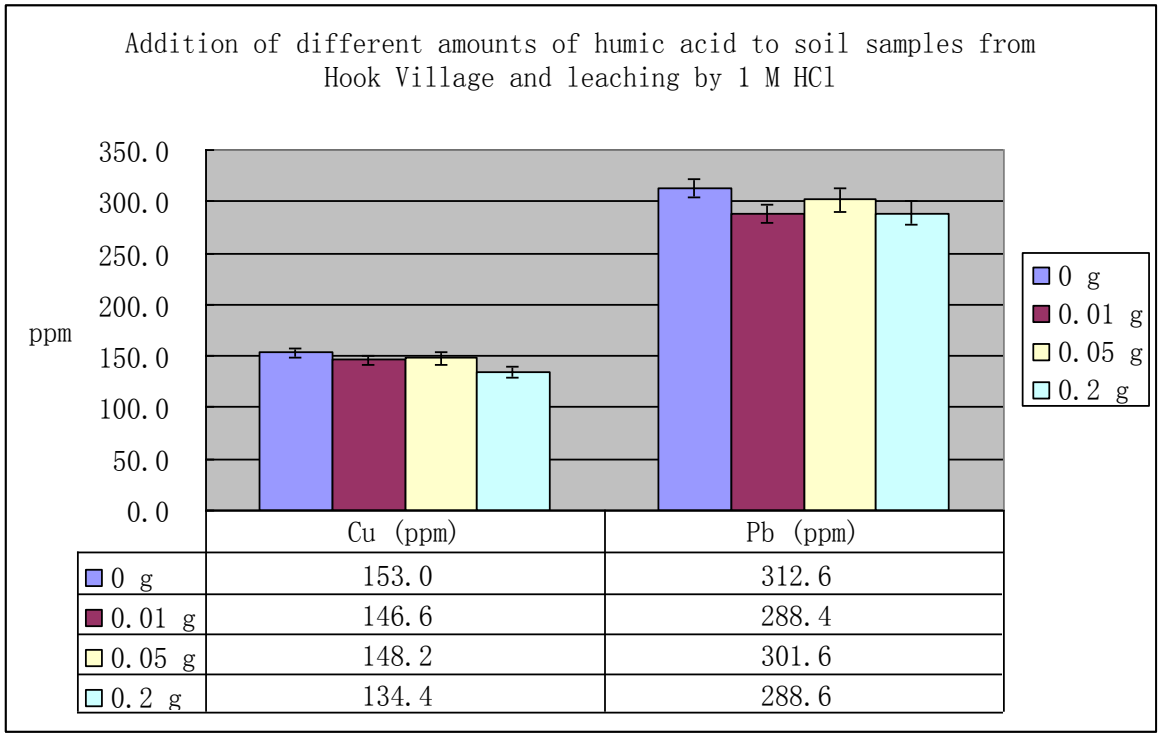
$$HA + H^+ \leftrightharpoons H_2A^+$$

In 1976, Stevenson showed that humic substances have a special feature that they exhibit buffering over a wide pH range [3]. In this section, the buffer solution decreases the acidity of the leachate and affects the leaching results. In other words it is the HCl which is the dominant reagent in causing the leaching of metal ions here. The role of the humic acid in these experiments is simply to buffer the pH so that as more humic acid is added the pH rises. A pH measurement was made using a Jenway 3020 pH meter. The pH value for 0.05 M HCl is 1.30. When 0.01 g, 0.05 g and 0.2 g humic acid were added to 20 mL HCl solution (0.05 M) respectively, the pH values increase to 1.32, 1.37 and 1.74 respectively. It suggests that the concentration of the H^+ decreased from 0.05 M to 0.018 M. Thus smaller proportions of metal ions are extracted. It is noteworthy from the data presented in Table 6.3.2 and Figure 6.3.2.3 that there is little difference between the proportions of Cu and Pb ions extracted – in other words the curves for Cu and Pb in Figure 6.3.2.3 follow very similar paths. This provides further evidence that it is not the humic acid that is primarily responsible for the extraction of metals here. This hypothesis has been tested further in a series of experiments described in section 6.4. It is also noteworthy that humic acid will not bind strongly to metal ions at pH values between 1- 2. This is because the carboxylic acid groups are all in their prontonated form (see Table 6.1) at this pH.

6.3.3 Addition of different amounts of humic acid salt with 1 M HCl as the leachate

These leaching results observed using 0.05 M HCl are completely different from those from those using deionised water as the leachate. Further spiking experiments with more concentrated HCl were therefore carried out.

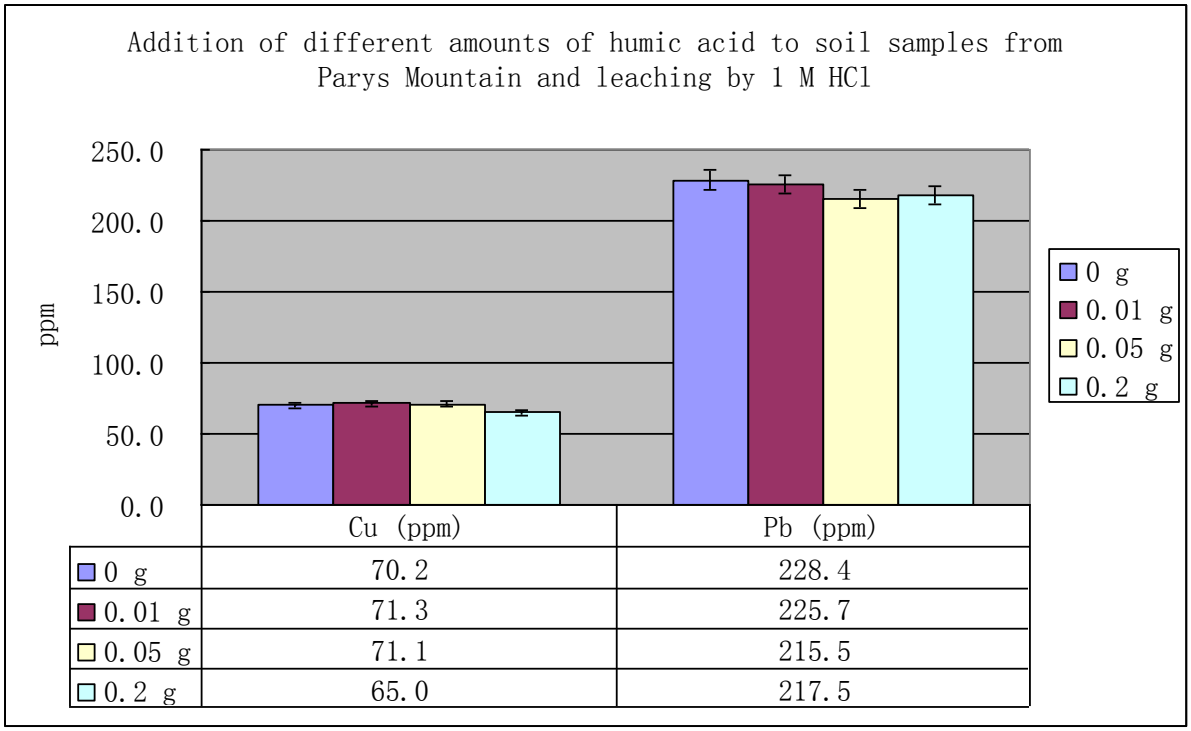
The soil samples from Hook Village and Parys Mountain were taken and to them were added different amounts of humic acid and then leaching was carried out using 20 mL 1 M HCl solution to get a comparison. To the samples from each site were added 0 g, 0.01g, 0.05 g and 0.2 g of humic acid respectively.



	Cu (ppm)	Pb (ppm)
0 g	153.0	312.6
0.01 g	146.6	288.4
0.05 g	148.2	301.6
0.2 g	134.4	288.6

Figure 6.3.3.1 Comparison of spiking experiments to determine the concentration of Pb and Cu leached by 1 M HCl solution while adding different amounts of humic acid (0 g , 0.01g, 0.05 g and 0.2 g) to the soil samples from Hook Village and detected by AAS

Figure 6.3.3.1 shows that when different amounts of humic acid were added to the soil samples from Hook Village and leached by 1 M HCl, the amount of both copper and lead leached from the samples does not change too much.



	Cu (ppm)	Pb (ppm)
0 g	70.2	228.4
0.01 g	71.3	225.7
0.05 g	71.1	215.5
0.2 g	65.0	217.5

Figure 6.3.3.2 Comparison of spiking experiments to determine the concentration of Pb and Cu leached by 1 M HCl solution while adding different amounts of humic acid (0 g , 0.01g, 0.05 g and 0.2 g) to the soil samples from Parys Mountain and detected by AAS

From Figure 6.3.3.2, the leaching results from Parys Mountain samples are quite similar to those from Hook Village samples. Adding more humic acid to the soil samples does not affect the leaching results for copper and lead.

Table 6.3.3 Percentages of Cu and Pb from soil samples leaching by 1 M HCl while adding different amounts of humic acid and detected by AAS and compared with the results of original soil samples determined by XRF

Mass of humic acid / g	Cu-Hook	Pb-Hook	Cu-Parys	Pb-Parys
0 g	68.00 %	82.58 %	73.23 %	86.69 %
0.01 g	65.15 %	76.20 %	74.40 %	85.67 %
0.05 g	65.86 %	79.68 %	74.19 %	81.80 %
0.2 g	59.75 %	76.24 %	67.81 %	82.53 %

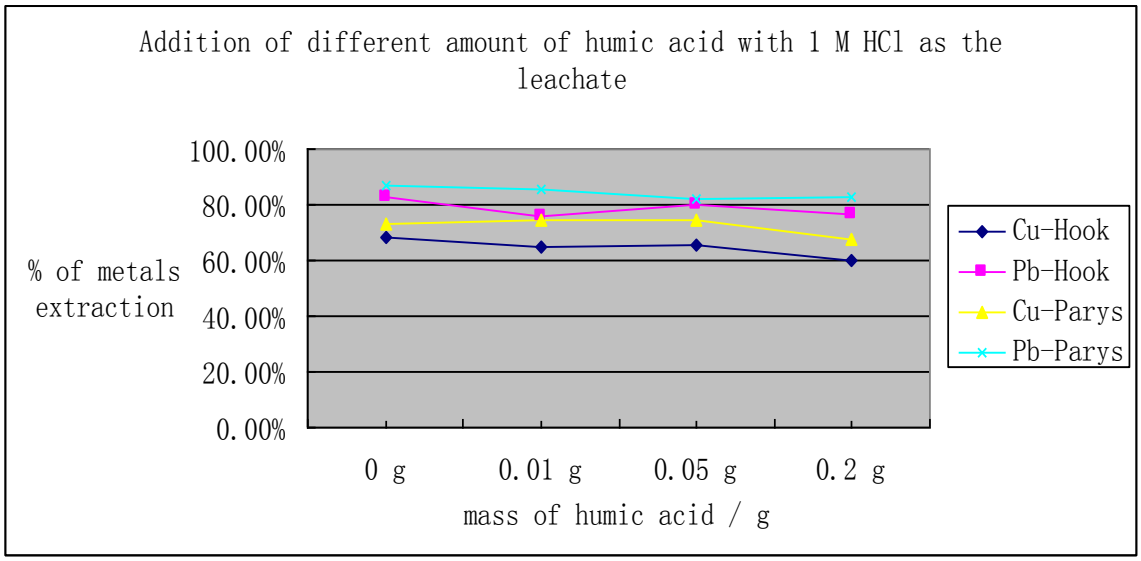


Figure 6.3.3.3 Percentages of Cu and Pb from soil samples leaching by 1 M HCl while adding different amounts of humic acid and detected by AAS

From Table 6.3.3 and Figure 6.3.3.3 above, the trend line of Cu and Pb leached out by 1 M

HCl with different amounts of humic acid from both two sites is nearly horizontal.

6.4 Uv-vis Spectroscopy

In step 6.3.2, it is shown that when 0.2 g of humic acid is added to soil samples and when using 0.05 M HCl as leachate, the leaching results for both Cu and Pb show a clear decrease. The reason may be that humic acid reacts with diluted HCl and forms a buffer solution.

A simple experiment has been carried out to attempt to confirm this hypothesis. Soil samples from Hook Village and Parys Mountain have been taken and leached by 20 mL 0.05 M HCl solution. The leachates were passed through a column with 10 g sand (Fisher, Sand - low iron, SiO_2, CAS:14808-60-7) and 400 mg humic acid (Sigma-Aldrich, CAS:145-93-6) and eluted by 0.05 M HCl. Ultraviolet-visible spectroscopy was used to verify whether there is humic acid in the fractions and atomic absorption spectroscopy was used to detect the metal concentrations in each fraction.

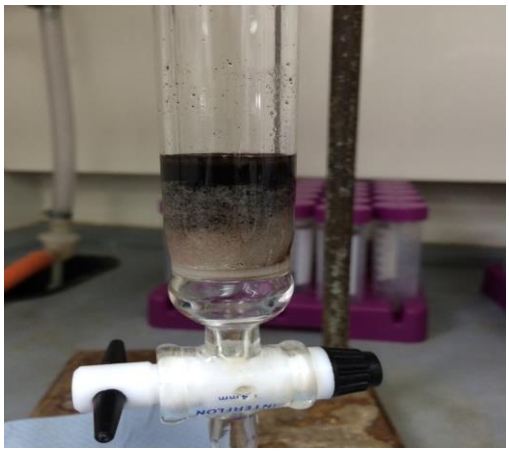


Figure 6.4.1 column with 10g sand and 400 mg humic acid

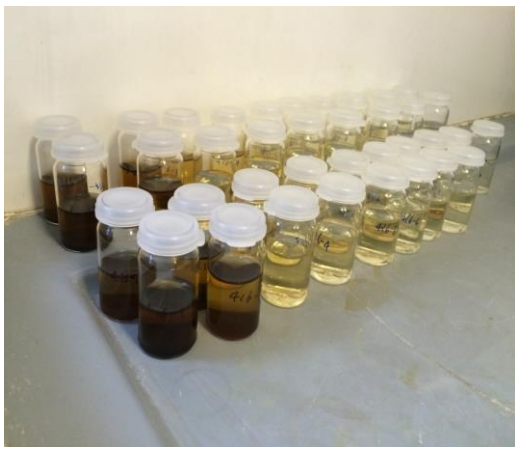


Figure 6.4.2 fractions of leachates through the special column

The metal concentrations of all of the fractions are too low to detect by AAS after eluting by 0.05 M HCl. However, it is clear from the picture in Figure 6.4.2 that the humic acid (which is coloured brown) is present in a number of discreet fractions – those which elute most quickly. The UV-visible spectra of the first fraction from different sites eluted are shown in Figure 6.4.4 and 6.4.5 and are compared with a UV-visible spectrum of humic acid (Figure 6.4.3). Instrumental difficulties led to the spectra being of rather low resolution.

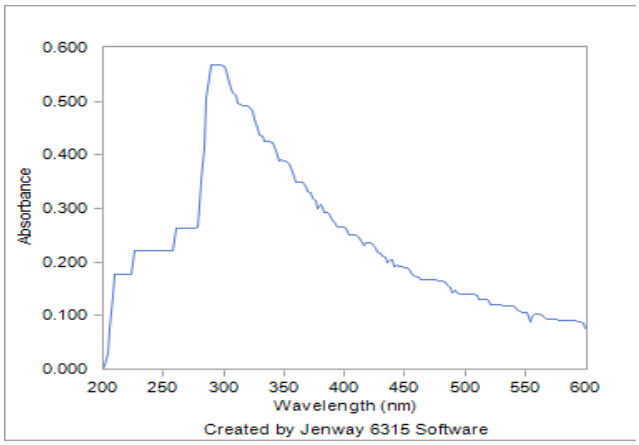


Figure 6.4.3 UV spectrum of humic acid (40 mg / L)

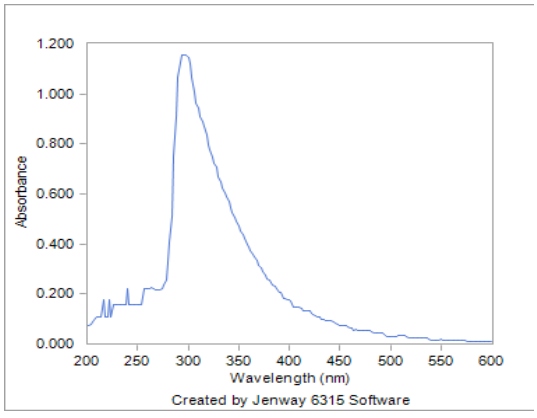


Figure 6.4.4 UV spectrum of fraction sample 1 from Hook village and diluted 20 times

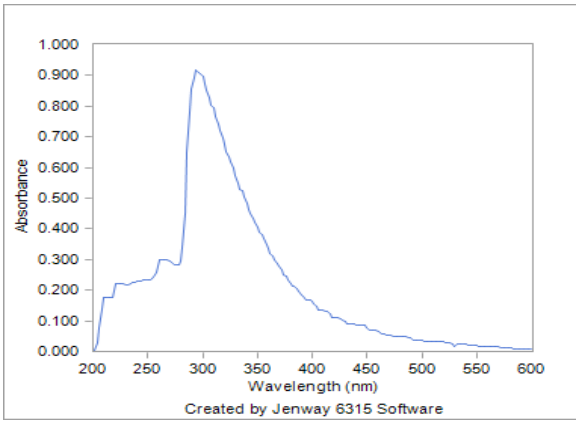


Figure 6.4.5 UV spectrum of fraction sample 2 from Parys Mountain and diluted 15 times

From the three figures above, it is easy to find that for the standard humic acid solution, there is a peak between 300-350 nm [4, 18]. The peak can also be found in the first two fractions eluted from samples from Hook Village and Parys Mountain.

It is clear from these results that humic acid and Cu or Pb ions are not forming a soluble (leachable) complex when dilute HCl is added. If a complex were formed then high metal concentrations would be expected to be seen in the fractions where high humic acid concentrations are also observed. This is not the case. The metal ion concentration is low in all fractions whereas some fractions (those eluted very quickly) show high humic acid concentrations.

6.5 Discussion and Conclusion

In this chapter, several experiments have been done to investigate the effect of humic acid in affecting the leaching of metal ions from the soil samples.

Firstly, it was found that the soil samples from both Hook Village and Parys Mountain contain humic acid. And the Hook Village samples have more humic acid (7.9 %) than the Parys Mountain samples (2.1 %).

Secondly, some “spiking” experiments have been done to investigate the effects of humic acid on the leaching experiments. Three different matrices (deionised water, 0.05 M HCl and 1 M HCl) have been selected to do the leaching experiments. Different amounts of humic aicd (0 g, 0.01g, 0.05 g and 0.2 g) were added to soil samples. The humic acid was found to have very different effects when using different matrices. The leaching results for Hook Village and Parys Mountain have very similar tendencies, so here just two figures from Hook Village are shown as an example.

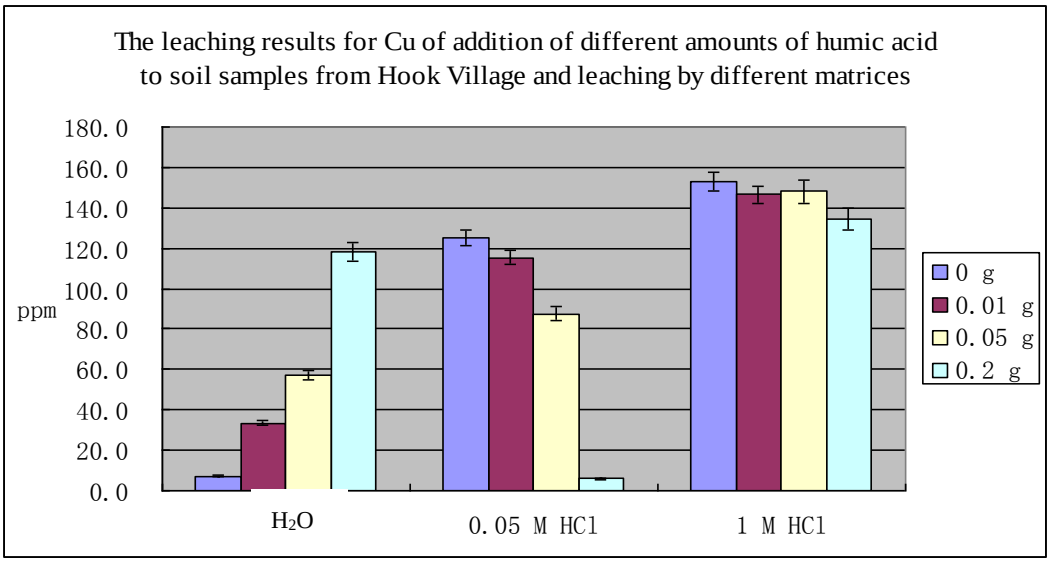


Figure 6.5.1 Comparison of spiking experiments to determine the concentration of Cu leached by deionised water, 0.05 M HCl and 1 M HCl while adding different amount of humic acid (0 g , 0.01g, 0.05 g and 0.2 g) to the soil samples from Hook Village and detected by AAS

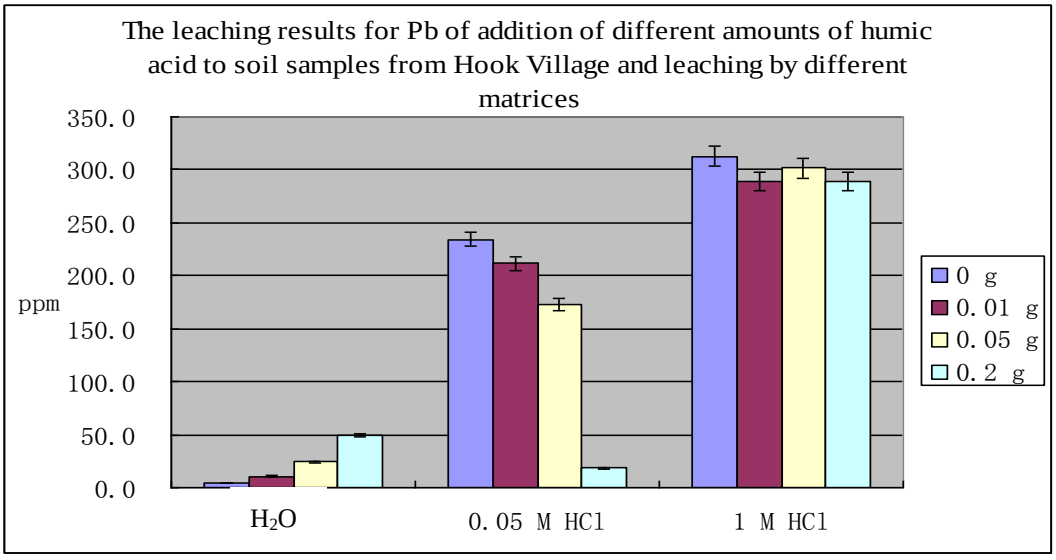


Figure 6.5.2 Comparison of spiking experiments to determine the concentration of Pb leached by deionised water, 0.05 M HCl and 1 M HCl while adding different amount of humic acid (0 g, 0.01g, 0.05 g and 0.2 g) to the soil samples from Hook Village and detected by AAS

Comparing Figure 6.5.1 and Figure 6.5.2, some interesting conclusions can be found:

1. Humic acid has a positive effect on leaching of metals when the matrix is deionised water.

2. When using deionised water as matrix, copper ions form a complex with higher stability than do lead ions.

3. Humic acid can react with 0.05 M HCl and under these conditions it acts as a buffer. Under these conditions addition of humic acid decreases the amount of metal ions leached from the soil samples.

4. When more concentrated HCl (1 M) is used as the leachate the addition of humic acid does not make much difference to the proportion of Cu or Pb ions leached from the samples.

It is possible to explain these results as follows:

Humic acid forms complexes with both Cu and Pb ions. When deionised water is used as leachate addition of humic acid promotes the leaching of these metal ions from the sample. Copper ions are leached more efficiently than lead ions by humic acid under the conditions of these experiments.

When dilute HCl is added the dominant effect is that the acidity of the HCl leads to leaching of the Cu and Pb ions. However, addition of humic acid buffers the HCl and hence addition of humic acid actually *decreases* the amount of Pb and Cu ions leached form the samples.

When more concentrated HCl (1 M) is added it is still the case that it is the HCl that is the dominant reagent in causing leaching of the Cu and Pb ions. Now, however, the HCl is too concentrated for the humic acid to have much of a buffering effect and so the amount of Cu and Pb ions leached from the samples does not change much as the amount of humic acid

added to the sample increases.

These results show that humic acid can play an important role in the leaching of metal ions from soil samples but that in fully understanding its chemistry it is important to consider other factors such as the pH of the sample.

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Chapter 7 Conclusions

In this research, a wide range of analytical experiments have been carried out to determine the composition of the soil samples from two polluted mining areas: Hook Village and Parys Mountain and to investigate the effect of chemical leaching of heavy metals from soil samples.

To determine the composition of the soil samples, different analytical methods and techniques have been used including thermal analysis, pH measurement, infrared spectroscopy, X-ray fluorescence spectroscopy, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry and particle size analysis. The following Table 7.1 shows the overall of the samples.

Table 7.1 Properties of the soil samples from Hook Village and Parys Mountain

		Hook Village	Parys Mountain
Water content (%)		3.41 % ± 0.025 %	1.41 % ± 0.039 %
Organic content (%)		9.07 % ± 0.17 %	4.41 % ± 0.38 %
Carbonate content (%)	pure $CaCO_3$	3.10 % ± 0. 43 %	1.45 % ± 0.38 %
	pure $MgCO_3$	2.60 % ± 0. 36 % c	1.21 % ± 0.32 %
pH value	0.5 g + 20 mL H_2O	6.12 ± 0.06	7.40 ± 0.06
	2 g + 20 mL H_2O	5.18 ± 0.10	7.24 ± 0.11

From Table 7.1 above, the results of XRF and thermal analysis show that the carbonate content of the soil samples is actually a mixture of calcium and magnesium carbonates so the actual carbonate content will be somewhere between the values calculated for pure $CaCO_3$ and pure $MgCO_3$.

Infrared Spectroscopy (IR) has been done to identify some of the minerals present in the soil samples. Quartz and clay minerals are present in both samples. Parys Mountain may contain a sulphate-containing mineral, probably barite ($BaSO_4$) or gypsum ($CaSO_4$). There is also evidence of $CaCO_3$ or $MgCO_3$ in the samples studied here which is characterized by bands around 1409 cm^{-1} from the asymmetric stretching of the carbonate ion.

XRF has been done to determine which specific metals contaminate the soils and the concentrations of these metals in each sample. This work also allowed which elements should be selected for leaching experiments. Si and Al are found from both sites samples in a high level (Hook Village: Al: 7.56±0.06 %, Si: 32.25±0.17 %, Parys Mountain: Al: 2.42± 0.12 %, Si: 39.15±1.04 %). Both sites' samples contain varying degrees of K, Na, Mg and Ti and the soils also have varying trace quantities of Cr, Co and Ni. As Parys Mountain is known to be a major copper-mining area, its concentration of copper (95.8 ppm) is nearly four times higher than the mean value for the whole of Wales (23.23 ppm). There is an interesting finding that the Hook Village samples show higher levels of copper (225.0 ppm) than the Parys Mountain samples. Hook Village was a coal mining area in the 19th century. This may simply mean that coal mining activity can lead to more pollution and the mining work in Parys Mountain has been efficient at extracting the copper before adding the waste to the spoil tips. From the report of UK soil and Herbage pollutant Survey report No. 7 from The Environment agency [32], concentrations of copper, zinc and lead in rural soils of Wales have mean values of 23.23 ppm, 87.9 ppm and 59.2 ppm, respectively and the average concentration of iron, copper, zinc and lead of Hook Village and Parys Mountain contained significantly higher levels than this. The following Table 7.2 shows the average concentration of iron, copper, zinc and lead of the two sites and these four metals were selected as representative metals to study in leaching experiments.

Table 7.2 Average concentration of four metals (Fe, Cu, Zn and Pb) in soil samples from Hook Village and in Parys Mountain determined by XRF

	Fe	Cu	Zn	Pb
Hook Village	4.69 ± 0.11%	225 ±2.2 ppm	309 ±4.2 ppm	379 ±6.1 ppm
Parys Mountain	2.56 ± 0.03 %	96 ±5.9 ppm	103 ±3.2 ppm	264 ±25.5 ppm

Leaching tests are fundamental tools for the assessment of contaminated soil. Leaching experiments have played an important role in this research. Different acids and different concentrations of acids were used as matrices to extract heavy metals from the soil samples. Chelating agents such as EDTA were also selected to compare with the acidification process. The leaching results of heavy metals can be compared with the results from XRF which give the overall concentrations of metal in the soils. In this research, it is also shown that chemical parameters can affect the leaching results. Ground and unground samples were used as a control test with the same leaching process to compare the leaching results. It is found that higher concentrations of metals are leached from the ground samples.

Atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) were used to analyse leachate solutions and get a comparison. The leaching results of Cu, Zn and Pb from ICP-MS are generally similar to the results from AAS. However, there are some differences between the results from AAS and ICP-MS. The reason may be when the leachates diluted 100 times to determine by ICP, the big dilution factor may add some errors. This finding, however, that generally AAS and ICP-MS give similar results gives confidence in the robustness of the method and the accuracy of the results obtained.

The following four figures show the concentrations of Cu, Zn, Pb and Fe leached from Hook Village using different acids and EDTA-2Na as matrices and detected by AAS. These values are compared with the overall concentration of the metal in the soil samples detected by XRF.

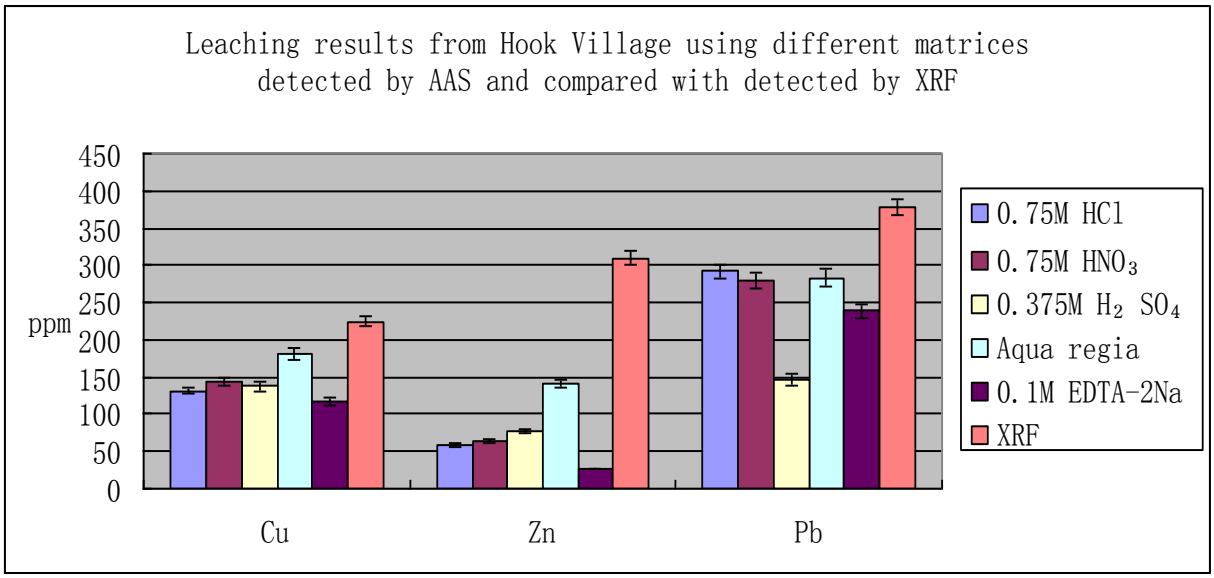

Figure 7.1 A graph showing the concentrations of Cu, Zn and Pb leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, Aqua regia and 0.1 M EDTA-2Na as matrices and detected by AAS and soil samples detected by XRF

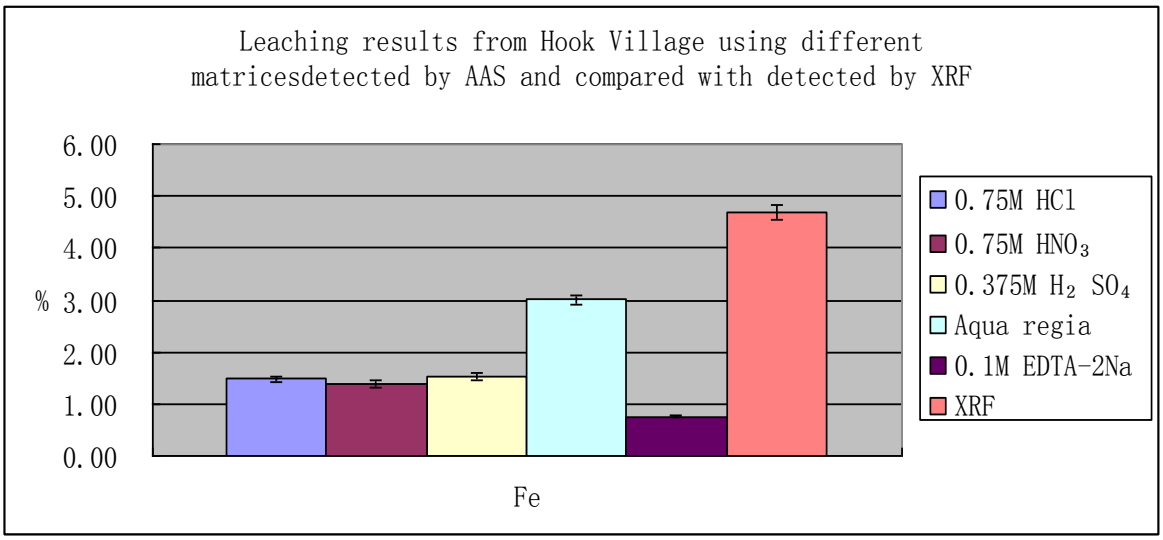

Figure 7.2 A graph showing the percentage of Fe leached from Hook Village using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, Aqua regia and 0.1 M EDTA-2Na as matrices and detected by AAS and soil samples detected by XRF

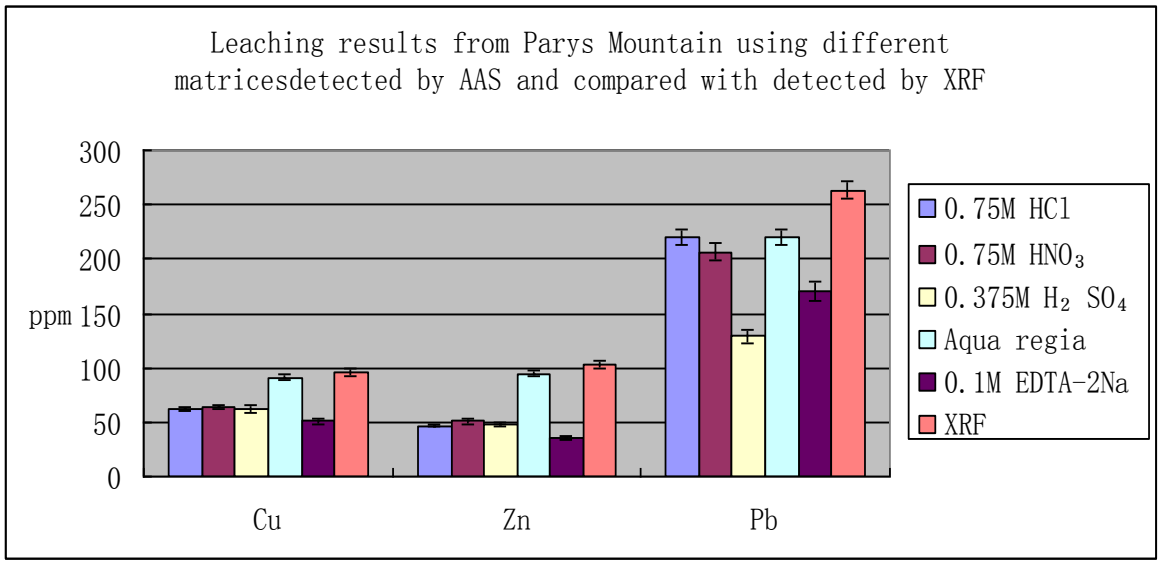

Figure 7.3 A graph showing the concentrations of Cu, Zn and Pb leached from Parys Mountain using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, Aqua regia and 0.1 M EDTA-2Na as matrices and detected by AAS and soil samples detected by XRF

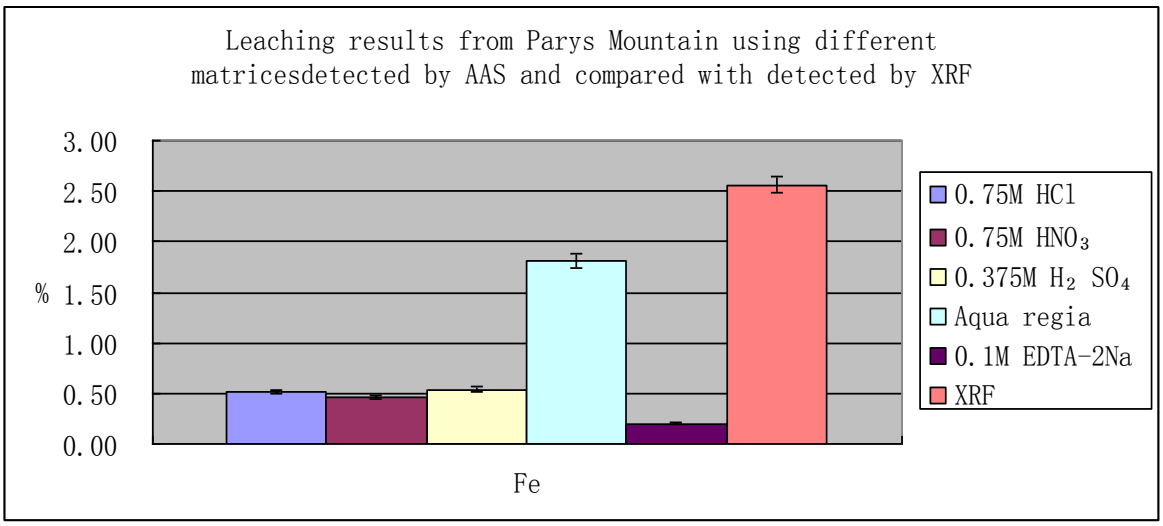

Figure 7.4 A graph showing the percentage of Fe leached from Parys Mountain using 0.75 M HNO_3, 0.75 M HCl, 0.375 M H_2SO_4, Aqua regia and 0.1 M EDTA-2Na as matrices and detected by AAS and soil samples detected by XRF

Four different acids (aqua regia, hydrochloric acid, sulfuric acid and nitric acid) and different concentrations of these acids have been used to carry out leaching experiments for the soil samples. And the leaching results have been compared with the XRF results. Some interesting conclusions have been found:

All these four acids can leach out Pb, Zn, Cu and Fe from the soil samples but not all of the heavy metals can be leached out.

Aqua regia is a very strong acid and can extract a higher proportion of the metals than the other three acids.

HCl, H_2SO_4 and HNO_3 solution are good matrices for leaching experiments, but when the acids have a similar pH value, they have different efficacies of soil leaching.

The amount of metal leached from one of the soil samples does not always increase as the acidity increases.

The lead leaching results gave a curve which showed no obvious trend when using increasing concentration of H_2SO_4 solution.

Because of the low solubility of lead sulfate, the higher concentrations of sulfuric acid do not necessarily lead to the extraction of more lead. The leaching results of Pb using different concentrations of H_2SO_4 show a "waving" curve. It may because $PbSO_4$ is very slightly soluble in water, so that the increasing of H^+ ion concentration may enhance positive effects of the solubility of lead compound while the increasing of SO_4^{2-} concentrations may lead to more $PbSO_4$ precipitation. The relevant equations are:

$$H_2SO_4\,(aq) \rightleftharpoons HSO_4^-\,(aq) + H^+\,(aq),$$

$$HSO_4^-\,(aq) \rightleftharpoons SO4^{2-}\,(aq) + H^+\,(aq),$$

$$Pb^{2+}\,(aq) + SO_4^{2-}\,(aq) \rightarrow PbSO_4\,(s)$$

A spiking experiment has been carried out to confirm this hypothesis. When different amounts of $CaSO_4$ and Na_2SO_4 were added into the soil samples, the more sulfate was added, the less Pb ions can be leached out.

Different chelating agents (0.1 M EDTA-2Na, 0.1 M EDTA-4Na and 0.005 M DTPA) have also been used to carry out leaching experiments to investigate the efficiency of chelating agents.

The results show that both EDTA-2Na and EDTA-4Na can extract heavy metals from soil samples but for different metals, they have different efficiency. For zinc and copper, the amount of metals leached out by the two EDTA salts is quite similar. For iron ions, EDTA-2Na can leach more than EDTA- 4Na solution. But EDTA-4Na is better at leaching lead ions. One reason may be the different metal sizes have some relationship with leaching results as Pb^{2+} is the largest cation in those four metals. Another reason may be that the pH conditions affect the leaching results as the pH value for 0.1 M EDTA-2Na

solution is nearly 4 while the pH value for 0.1 M EDTA-4Na solution is nearly 11. To verify this hypothesis, a control group leaching experiment (0.1 M EDTA-4Na under different pH conditions) was carried out to investigate whether the pH value of the EDTA sodium salt affects the leaching results. The experiment shows that under alkaline conditions it is easier to combine lead ions with EDTA salts. The results confirm that the precise pH conditions are important and that different metals may be leached more efficiently from soils at different pH values.

Some "spike" experiments have been done to compare with the results when using inorganic acids as matrices. When using H_2SO_4 as matrix, the more $CaSO_4$ is added into the soil samples, the less Pb ions can be leached out. But when using EDTA-2Na as matrix, even when different amounts of calcium salts were added into the soil samples, does not affect the leaching results very much. It suggests that EDTA is more efficient to combine with Pb^{2+} than SO_4^{2-} and so in the presence of EDTA Pb^{2+} ions preferentially bind with the EDTA to form a complex rather than precipitating with the SO_4^{2-} ions. In other words the presence of EDTA enhances the solubility of $PbSO_4$.

As humic acid is widespread on the Earth's surface, this research also investigated the role of humic acid in the leaching of metals from soils. It was found that the soil samples from both Hook Village and Parys Mountain contain humic acid. Hook Village samples have more humic acid (7.9 %) than the Parys Mountain samples (2.1 %) and the reason may that Hook Village was a coal mining area in the past which has led to more humic acid in the soil samples.

From the experiments described in chapter 6, it is confirmed that humic acid has a positive effect on leaching of metals when the matrix is deionised water. It can form complexes with both Cu and Pb ions but copper are leached more efficiently than lead ions. When using diluted HCl as a matrix, the dominant effect is that the acidity of the HCl leads to leaching of the Cu and Pb ions. However, addition of humic acid buffers the HCl and hence addition of humic acid actually decreases the amount of Pb and Cu ions leached form the samples. When more concentrated HCl (1 M) is added it is still the case that it is

the HCl that is the dominant reagent in causing leaching of the Cu and Pb ions. Now, however, the HCl is too concentrated for the humic acid to have much of a buffering effect and so the amount of Cu and Pb ions leached from the samples does not change much as the amount of humic acid added to the sample increases. These results show that humic acid can play an important role in the leaching of metal ions from soil samples but that in fully understanding its chemistry it is important to consider other factors such as the pH of the sample.

For future work, more experiments could be done to identify the mineral composition of the soil samples. As the results in Figure 7.1 indicate, it is found that less than half of the zinc ions can be extracted by acid or a chelating agent. It would be very interesting to investigate the exact mineral content. This could be done, in principle, by a combination of powder X-ray diffraction and infrared spectroscopy backed up by the use of a mineralogical microscope. However, such experiments may not be straightforward. As noted in this thesis X-ray diffraction patterns tend to be dominated by the most crystalline components e.g. quartz and it is notoriously difficult to detect components at low concentrations (less than about 10%) by powder X-ray diffraction. Infrared spectroscopy is useful but again it can be difficult to identify minor components using this technique. The mineralogical microscope is a useful tool but does not directly give chemical information. These experiments would be useful but, as noted, not necessarily easy to perform. It would also be interesting to detect and identify the organic pollutants in the soil samples. This could be done by chromatography-mass spectrometry methods (e.g. HPLC). Such studies might allow more leaching agents such as organic acids to be identified.

Finally, the work in this thesis establishes a principle that there is much interest in looking at fundamental physical chemistry processes when studying the leaching of metal ions from soil samples. However, the time constraints of a single PhD study have allowed only two sites to be studied. It would be very useful to extend the study to more sites. In particular sites with different mining histories, sites with different concentrations of metal ions, sites with different organic content of soils and sites with different mineralogy could

be explored. It would also be useful to extend these laboratory studies by carrying our field work in order to see how applicable the data obtained in the laboratory is to the field. For example the effects of acid mine drainage where typically quite high concentrations of sulfuric acid may be found (formed by oxidation of sulfide minerals) on the leaching of metals could be explored in a field survey.

Appendix

Appendix 1

Raw Data for determination of water content by thermal analysis

Table 1 Water content of soil samples studied as determined by thermal analysis at 105 °C

Site	Mass of sample (g)	Mass after heating for 24 h (g)	Mass after heating for 48 h (g)	Mass after heating for 72 h (g)	Mass after heating for 96 h (g)	Mass after heating for 168 h (g)	mass loss on heating %
Hook1	18.6971	18.1013	18.0832	18.0793	18.0710	18.0618	3.40
Hook2	19.5904	18.9683	18.9508	18.9478	18.9397	18.9268	3.39
Hook3	19.1807	18.5610	18.5461	18.5426	18.5342	18.5205	3.44
Hook4	19.9402	19.2991	19.2843	19.2806	19.2713	19.2551	3.44
Hook5	19.9351	19.2971	19.2839	19.2800	19.2697	19.2539	3.42
Hook6	20.4301	19.7918	19.7709	19.7653	19.7590	19.7434	3.36
Hook7	19.259	18.6505	18.6332	18.6292	18.6211	18.6066	3.39
Hook8	19.5646	18.9449	18.9275	18.9244	18.9155	18.8990	3.40
Hook9	18.4633	17.8746	17.8596	17.8555	17.8478	17.8351	3.40
Hook10	19.0458	18.4352	18.4202	18.4160	18.4093	18.3926	3.43
Parys1	25.3944	25.0555	25.0481	25.0427	25.0454	25.0412	1.39
Parys2	25.1903	24.8571	24.8505	24.8457	24.8494	24.8439	1.38
Parys3	25.169	24.8279	24.8197	24.8155	24.8195	24.8127	1.42
Parys4	24.8453	24.5091	24.5043	24.4986	24.5004	24.4942	1.41
Parys5	24.8045	24.4655	24.4606	24.4437	24.4455	24.4368	1.48
Parys6	25.4833	25.1373	25.1307	25.1248	25.1273	25.1212	1.42

Parys7	26.8015	26.4584	26.4527	26.4474	26.4496	26.4427	1.34
Parys8	25.7316	25.3911	25.384	25.3788	25.3744	25.3722	1.40
Parys9	25.9402	25.5894	25.5827	25.5768	25.5793	25.5672	1.44
Parys10	26.0118	25.6549	25.6491	25.6427	25.6452	25.6346	1.45

Appendix 2

Infrared Spectroscopy

Soil samples from Hook Village:

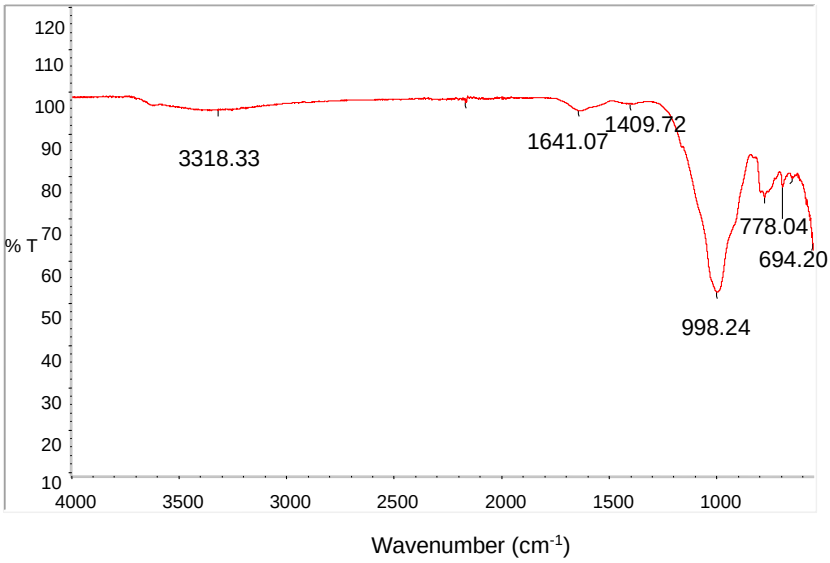

Figure 1 Infrared spectrum of dried soil sample 1 from Hook Village

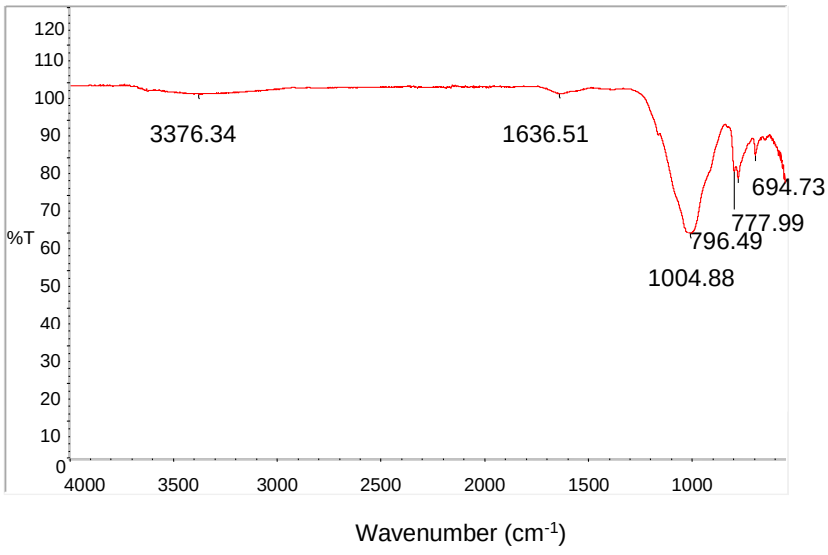

Figure 2 Infrared spectrum of dried soil sample 2 from Hook Village

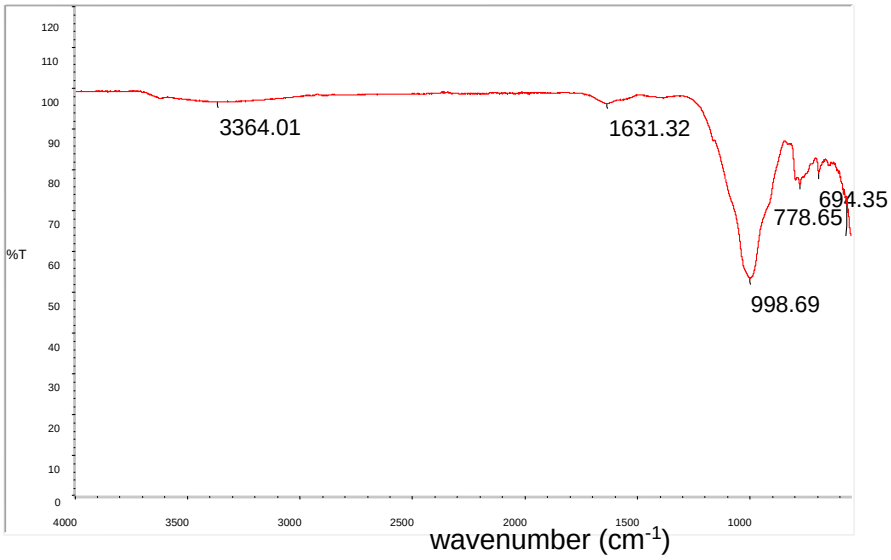

Figure 3 Infrared spectrum of dried soil sample 3 from Hook Village

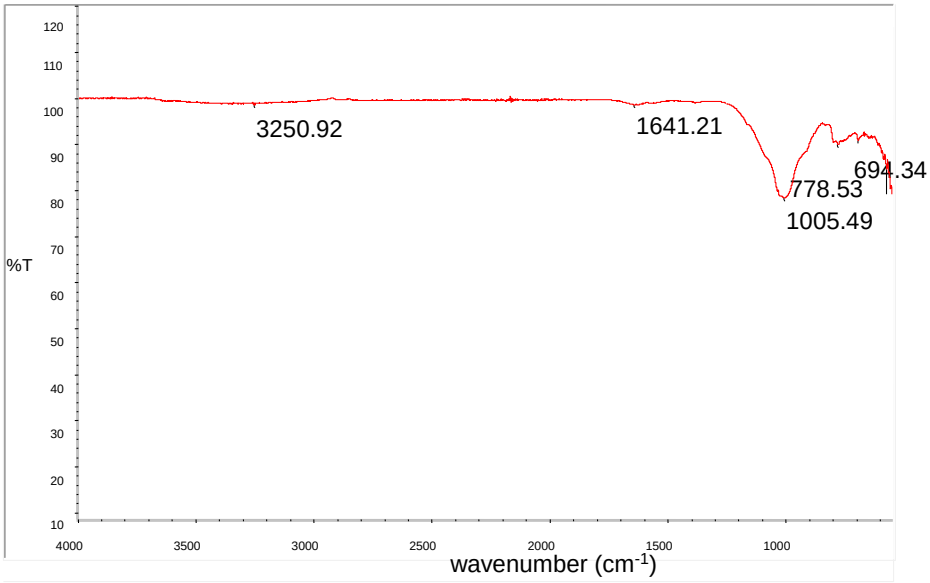

Figure 4 Infrared spectrum of dried soil sample 4 from Hook Village

Soil samples from Parys Mountain:

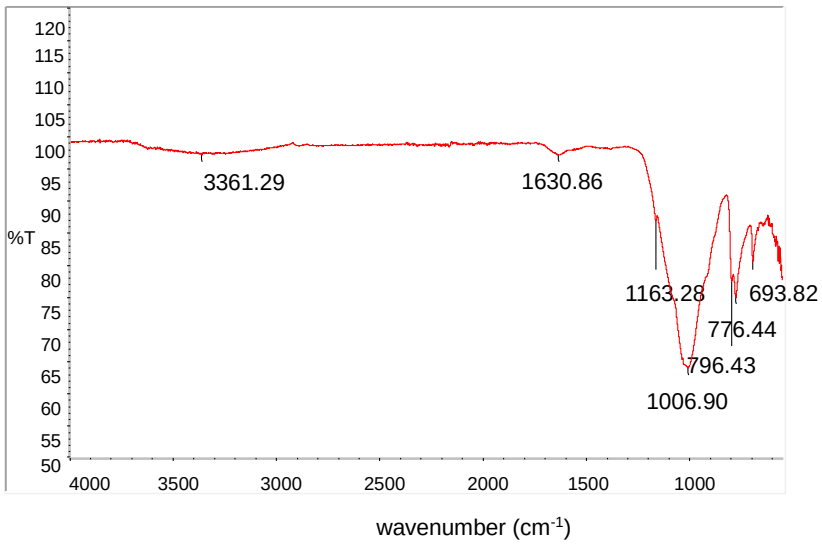

Figure 5 Infrared spectrum of dried soil sample 1 from Parys Mountain

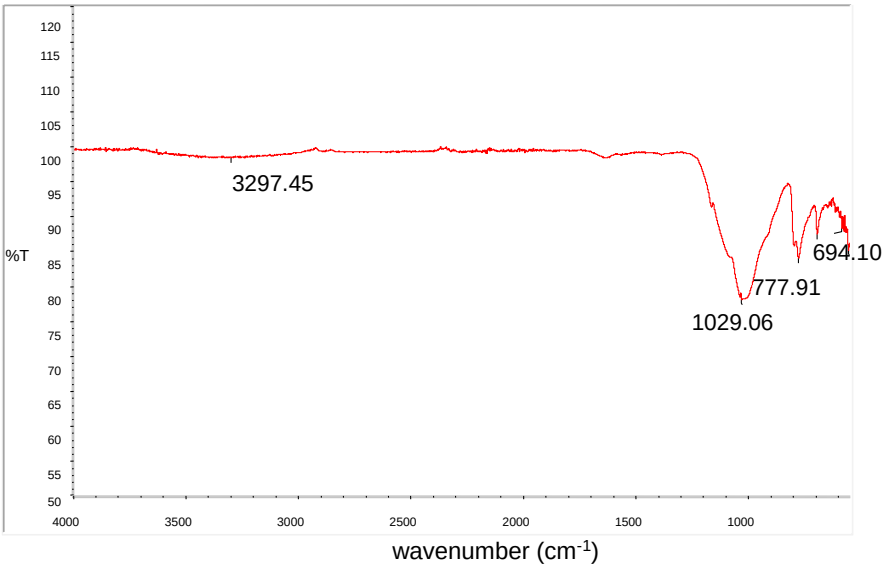

Figure 6 Infrared spectrum of dried soil sample 2 from Parys Mountain

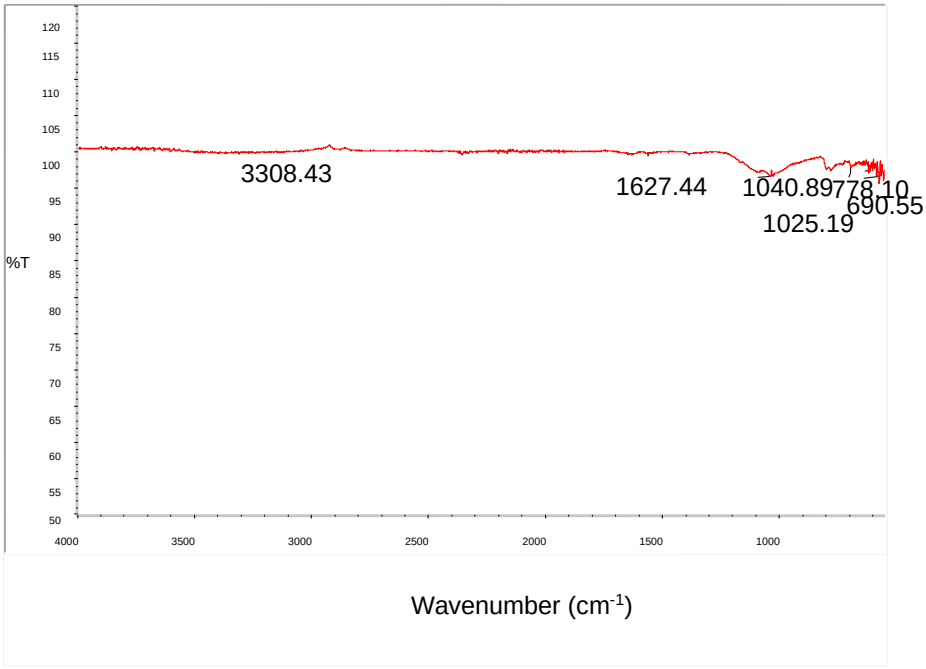

Figure 7 Infrared spectrum of dried soil sample 3 from Parys Mountain

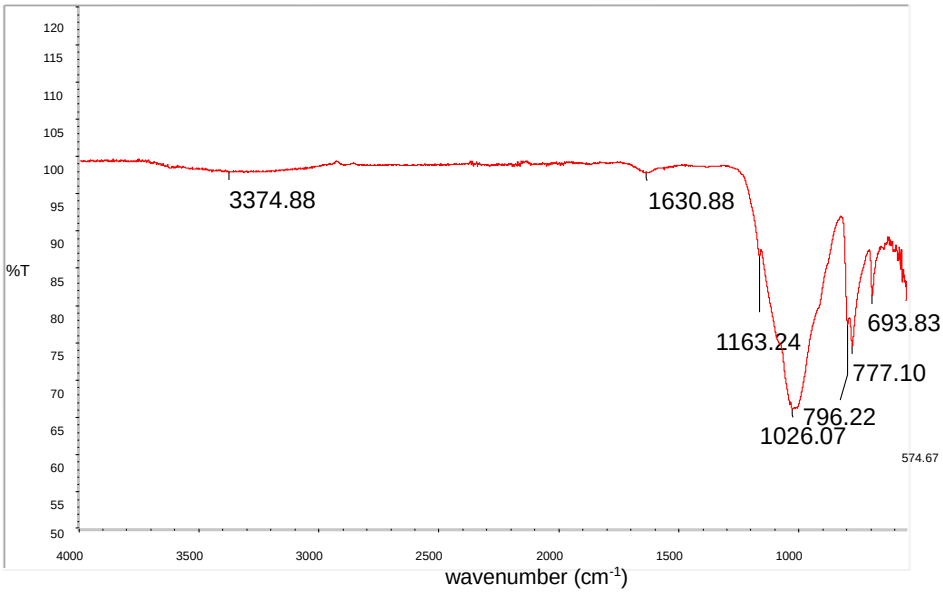

Figure 8 Infrared spectrum of dried soil sample 4 from Parys Mountain

Appendix 3

Raw Data for elements of soil samples from Hook Village and Parys Mountain determined by X-ray Fluorescence:

Table 2 Percentages of elements of soil samples from Hook Village and Parys Mountain determined by X-ray Fluorescence

Sample name	Hook 1	Hook 2	Hook 3	Hook 4	Parys 1	Parys 2	Parys 3	Parys 4
Metal name	%	%	%	%	%	%	%	%
Na	0.697	0.705	0.735	0.697	0.052	0.067	0.067	0.059
Mg	0.714	0.714	0.720	0.726	0.180	0.216	0.228	0.228
Al	7.571	7.539	7.486	7.634	2.245	2.446	2.509	2.467
Si	32.256	32.363	32.382	32.009	40.623	39.018	38.215	38.743
P	0.227	0.223	0.218	0.231	0.105	0.114	0.122	0.122
K	1.809	1.801	1.792	1.817	0.913	0.987	1.004	0.946
Ga	0.250	0.257	0.250	0.257	0.379	0.414	0.443	0.400
Ti	0.510	0.510	0.510	0.510	0.174	0.186	0.186	0.168
Mn	0.194	0.186	0.194	0.194	0.046	0.046	0.046	0.046
Fe	4.648	4.585	4.837	4.704	2.583	2.527	2.548	2.576

Table 3 concentrations of elements of soil samples from Hook Village and Parys Mountain determined by X-ray Fluorescence

Sample name	Hook 1	Hook 2	Hook 3	Hook 4	Parys 1	Parys 2	Parys 3	Parys 4
Metal name	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
V	122	115	115	111	26	36	20	24
Cr	84	78	83	80	38	42	41	34
Co	19	18	20	20	9	8	8	9
Ni	24	23	26	23	12	12	12	12
Cu	227	225	226	222	104	90	94	95
Zn	312	304	313	307	107	100	101	104
Rb	113	111	111	111	49	51	52	49
Sr	58	59	58	58	36	37	38	35
Y	31	31	30	32	14	14	15	15
Zr	277	280	274	272	257	281	292	239
Pb	383	371	384	376	286	229	260	279